



	Experiment title: Influence of pressure on hydrogen bonded polymers; polyamides and biopolymers	Experiment number: Sc1279
Beamline: ID11/ID02	Date of experiment: from: 15-19 Sept 2003 and 25-29 June 2004	Date of report: January 14 th 2005
Shifts: 9/12	Local contact(s): Guido Heunen/Peter Boesecke	<i>Received at ESRF:</i>
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Report:

Nylons (polyamides) often serve as well-controlled paradigms for examining the behaviour of biopolymers, in particular silk. In nylons and such materials, hydrogen bonding plays a prominent role both in crystallization and in melting, e.g. the interchain hydrogen bonding acts between neighbouring chains to form a sheet-like structure linked by weak van der Waals interactions; such properties give rise to the observed hardness and resiliency of nylons. The typical WAXD pattern of crystals of nylons shows strong reflections arising from the interchain and intersheet distances in the crystals. As the polymer is heated, the hydrogen bonding weakens at the so-called Brill transition and the interchain and intersheet spacings are observed to merge into a single reflection, by a transformation from the triclinic to the hexagonal phase. For nylon 4,6 the Brill transition occurs at approximately 190°C, well below the melting temperature of ~295°C.

In a test experiment nylon 4,6 was sealed in a glass tube in the presence of excess water and was heated. As the water is sealed in the tube, it is possible to heat the system above 100°C so that the water is in its superheated state but below its supercritical point and hence exhibits increased mobility and diffusion permeability. In this way, it was possible to dissolve the nylon below its melting point.

Using ID11 and ID02, the process of this dissolution of nylon in the presence of water (volume ratio 1:4) in a sealed glass ampoule has been studied. Initial studies used a flame sealed glass tube placed on the silver block of a Linkam heater. Subsequent experiments have used a new hot stage built at Eindhoven University for this specific application. By WAXD (ID11 and ID02), the nylon 4,6 as supplied (DSM, Stanyl) exhibited two broad crystalline reflections corresponding to the interchain and intersheet distances of 0.42 and 0.39nm, respectively (fig.1(a)). These values are very close to the high-temperature triclinic (monoclinic) phase identified in nylon 4,6. These reflections are superimposed on a broad halo attributed both to the water in the capillary as well as to amorphous nylon 4,6. As the solution is heated, the two crystalline peaks move closer together. At 100°C, the reflection associated with the interchain distance shows a sudden increase in intensity that may be due to reorganisation or perfecting (fig.1(b)). At around 190°C, the two crystalline reflections

merge into a single reflection, indicating a phase transition from the triclinic to the pseudo-hexagonal phase, the so-called Brill transition (fig.1(c)). On further heating, at $\sim 205^\circ\text{C}$, the well-defined single reflection disappears with a corresponding small increase in the amorphous halo, suggesting the complete dissolution of nylon 4,6 in water (fig.1(d)). Upon cooling, two reflections appear at 180°C , corresponding to the interchain and intersheet distances in the triclinic unit cell. Re-crystallization occurs directly in the triclinic phase without the intervention of the pseudo-hexagonal phase in contrast to re-crystallization from the melt, i.e. in the absence of water. On cooling further the reflections move further apart, the final solution being an opaque suspension of single crystals. The final d-spacings for interchain and intersheet distances at room temperature are 0.44 and 0.37nm, respectively, which are very close to the room-temperature (annealed) triclinic phase for nylon 4,6.

In another experiment, nylon 4,6 was dissolved in water in a sealed ampoule and heating continued until the temperature reached 245°C . The glass was unable to sustain the increased water vapour pressure and broke so evaporating the water. The nylon 4,6 immediately re-crystallised in the pseudo-hexagonal phase (being above the Brill transition temperature). Upon cooling, this now-dry sample recrystallised into the high-temperature, disordered triclinic phase as seen in nylon 4,6 which had not been exposed to water.

It is possible to extract the single crystals of nylon 4,6 from the cooled solution (fig.2). In this way, sedimented mats of the single crystals can be grown. The properties of these mats and their dissolution behaviour has also been examined using both ID11 and ID02.

In combination with other techniques, e.g. FTIR (fig.3) and NMR, it has been possible to conclude that the water-grown nylon 4,6 crystals have water intercalated within their crystal structure. Beamtime at the ILL has been granted to study these materials in nylons grown from D_2O in order to determine where the water actually sits within the crystalline lattice.

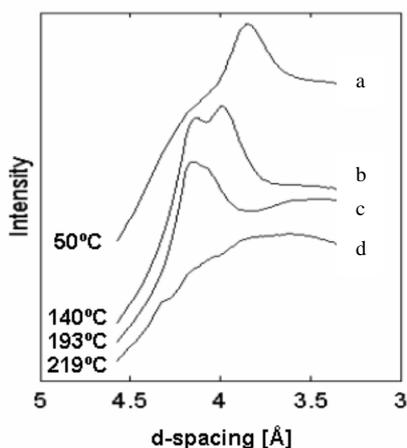


Fig.1: Series of WAXD diffraction patterns for nylon 4,6 and water (vol. ratio 1:4) sealed in a glass ampoule and heated

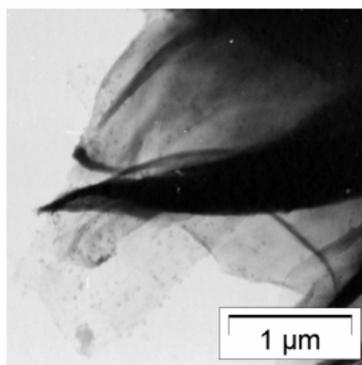


Fig.2: TEM micrograph of single crystals of nylon 4,6 sedimented after dissolution in water

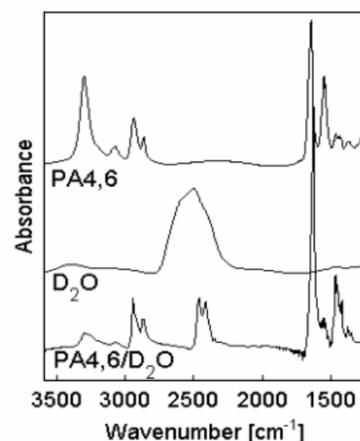


Fig.3: FTIR spectra for nylon 4,6, D_2O and nylon 4,6 dissolved in D_2O , revealing the possible intercalation of water within the nylon crystalline structure

Publications: 'Dissolution of Hydrogen-Bonded Polymers in Water: A Study of Nylon-4,6' S. Rastogi, A.E. Terry, E. Vinken, *Macromolecules*, 37(24), 8825-8828 (2004)

Posters: 'Dissolution of nylon in water: an in-situ X-ray study' Esther Vinken, Sanjay Rastogi, Ann Terry, 4th conference on Synchrotron Radiation in Materials Science, Grenoble 2004