Dissolution of Hydrogen Bonded Polymers in Water; From Synthetic to Biopolymers

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Summary: In several nylons, for example nylon 4,6, a transition occurs at elevated temperatures in which the hydrogen bonding between adjacent chains is most likely to weaken, the so-called Brill transition. In this communication the influence of superheated water on nylon 4,6 at and above the Brill transition temperature is investigated, superheating being achieved by increased vapour pressure upon heating water and nylon in a sealed glass capillary. From time-resolved X-ray studies it is shown that close to the Brill transition temperature, nylon 4,6 dissolves in water. Crystallization from the solution still under moderate pressures (~20bars) leads to the formation of single crystals. These crystals grow directly in the triclinic phase without the intervention of the pseudo-hexagonal phase. By Infrared spectroscopy we speculate that water intercalated within the confined geometry of the unit cell leads to a unique vibrational spectra. The trapped water exits from the unit cell above the Brill transition temperature, once the vapour pressure is released. These experimental findings are not limited to a specific polymer, but have implications for the dissolution of all hydrogen bonded polymers, irrespective of whether they are synthetic or biopolymers.

Introduction

At room temperature, ambient pressure crystalline structure of most nylons is formed from hydrogen bonded \( \beta \)-sheets linked by weak van der Waals interactions. It is this hydrogen bonding that plays a prominent role in both the crystallization and melting behaviour of these materials and also provides nylons their ubiquitous strength and intractability. However, Fourier Transform Infrared (FTIR) studies on nylon 10,10 have shown that with increasing temperature, there is a greater conformational disorder in the methylene segments and a weakening of the hydrogen bonding above the so-called Brill transition temperature. The Brill transition occurs in several nylons and has been shown by time-resolved wide-angle X-ray diffraction (WAXD) to be a crystalline transformation from a triclinic unit cell to a pseudo-hexagonal phase, the (100) reflection related to the interchain/intrasheet distance merging into the (010)/(110) intersheet reflection at this temperature. Crystallization conditions and the molecular weight influences the Brill transition temperature and lead to variations in published temperatures of nylon 4,6 in the range 180 to 250\(^\circ\)C. Furthermore, it is known that the triclinic interchain and intersheet distances are strongly affected by the crystal perfection, the conventional spacings of 0.44 and 0.37nm, respectively, only being achievable after annealing at elevated temperatures or upon solution crystallization.
Pressure is an important component that is present during the processing of polymers. Whilst in most materials pressure is known to increase the melting temperature, its influence on hydrogen bonding is not well understood. A well-known example is ice where hydrogen bonding plays a crucial role leading to an unusual melting point depression with increasing pressure. It is also well known that the vapor pressure of water increases on heating. Above 374°C and a vapor pressure greater than 220 bars, the supercritical region in the p-T water phase diagram is reached. However, above the ambient boiling point and below the supercritical point, water is in the superheated state where the hydrogen bonding between water molecules weakens considerably and the water molecules are highly mobile. Thus, in a polymer, for example nylon 4,6 where hydrogen bonding exists, the presence of water in its superheated state, and thus with enhanced diffusion permeability, can act as a solvent and leads to the complete dissolution of the nylon in water at elevated temperatures (>200°C). It is to be noted that at 200°C the water vapor pressure is approximately 20 bars.

**Experimental Section**

The polymer used in this study is a commercially available DSM produced nylon 4,6 (PA4,6), commonly known as Stanyl®. PA4,6 and water, in the ratio 1:4 by volume, were sealed in a glass capillary with inner diameter 1.5mm and length 10mm. The glass capillary was heated and cooled at 20°C/min using a Linkam TMS600 hotstage. Crystallographic changes were followed in-situ by means of WAXD at the Materials Science beamline (ID11) at the European Synchrotron Radiation Facility (ESRF), Grenoble. A 25KeV (\(\lambda = 0.4966\text{Å}\)) X-ray beam of size 300μm was used. 2-dimensional diffraction patterns were recorded every 20 seconds with a Bruker CCD detector for a 10 second exposure. Single crystals formed from the water solution were analyzed using a Philips Transmission Electron Microscope (TEM). GPC results show that in the given time for dissolution nylon does not hydrolyze. When left for more than 10 minutes the nylon 4,6 starts hydrolyzing at 220°C.

**Results and Discussion**

Figure 2 shows a series of WAXD patterns recorded during heating and cooling at 20°C/min for PA4,6/H2O in the volume ratio of 1:4 in a sealed glass capillary. At room temperature, the pattern shows two broad crystalline reflections corresponding to the interchain and intersheet distances for the triclinic phase of PA4,6, superimposed on a broad halo attributed to both the encapsulated water in the capillary as well as the amorphous PA4,6. As the mixture is heated, the two reflections move closer to each other, the interchain reflection contracting and the intersheet expanding. Figure 2(a), a characteristic feature of nylons. Around 100°C, the reflection associated to the interchain distance, shows a sudden increase in intensity that may be due to re-organization/crystal perfectioning. Since the encapsulated water in the capillary cannot escape, the water vapor pressure builds up with increasing temperature. Around 190°C the two crystalline reflections corresponding to the triclinic phase merge into a single reflection, indicating a phase transition from the triclinic to the pseudo-hexagonal phase, known as Brill transition. On further heating, at ~205°C, the well defined single reflection corresponding to the pseudo-hexagonal phase disappears with an increase in the amorphous halo suggesting the complete dissolution of PA4,6 in water. Upon cooling the PA4,6/H2O solution from the maximum temperature of 230°C, Figure 2(b) shows the reappearance of the two reflections at 180°C, corresponding to the intersheet and interchain distances in the triclinic unit cell, superimposed on an amorphous halo. The appearance of the two reflections 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 to room temperature the two reflections move further apart, the final solution being an opaque suspension of single crystals. Comparing the starting WAXD pattern for the PA4,6 in water prior to heating in Figure 2(a), with the final pattern following complete dissolution from Figure 2(b), it is still apparent that the interchain distance (0.44nm) in the PA4,6 crystallized from the water solution is at a higher d-value compared to the PA4,6 before heating as is the contracted intersheet distance (0.37nm). This distinction is clearly visible in Figure 2(e) for the diffraction patterns at 50°C. The re-crystallization from the water solution therefore occurs in a triclinic crystalline lattice closer to the room temperature triclinic phase for nylon 4,6. We would like to state once again that GPC results confirm that within the given time of the experiment molecular weight of PA4,6 remains unaltered. Figure 2c shows WAXD patterns recorded during the consecutive heating of this solution PA4,6/H2O crystals, still sealed within the glass capillary and hence in the presence of...
excess water. As anticipated, on heating the two reflections move closer to each other. However, no abrupt change in intensity or d-spacing (i.e. no high temperature triclinic phase) is observed at or above 100°C. At approximately the same temperature as in the first run, i.e. ~205°C, the two crystalline reflections suddenly disappear, leaving behind a broad halo similar to that observed at elevated temperatures and pressures in Figures 1(a) and (b). The Brill transition is at a higher temperature than for the initial run as the pseudo-hexagonal phase is not observed prior to dissolution. The capillary with a solution of PA4,6 and water was heated further. Vapor pressure increases with increasing temperature and at ~245°C, when the vapor pressure is anticipated to be approximately 36.5bars, the glass capillary can no longer withstand the pressure and breaks. Water at these high temperatures and now at atmospheric pressure evaporates from the capillary. The water-free PA4,6 at 245°C, i.e. much below its melting temperature (~295°C) crystallizes directly into the pseudo-hexagonal phase. The last three frames heating to a maximum temperature of 260°C in Figure 1(c) shows the crystallization of PA4,6 in the pseudo-hexagonal phase. It is to be noted that the single broad reflection at 0.42nm of the pseudo-hexagonal phase just after the Brill transition typically increases in intensity and becomes sharper with time. Figure 2(d) shows the consecutive cooling run of the PA4,6, now dry. At ~160°C, the single reflection splits into two corresponding to the Brill transition from the pseudo-hexagonal phase transforms into the triclinic phase. Due to the low Brill transition temperature we can conclude that the re-crystallization upon evaporation is highly disordered despite possible brief annealing at high temperatures and indeed the final interchain and intersheet distances are 0.42 and 0.40nm, respectively, i.e. the PA4,6 has re-crystallized in the high temperature triclinic phase.

Conclusions
From the series of X-ray diffraction patterns reported in Figure 2, it is evident that PA4,6 dissolves in water just above 200°C. It is also possible to re-crystallize the PA4,6 from this water solution. Fig 1(a) shows a typical Transmission Electron Micrograph of the PA4,6 crystals grown by the above process. The lath-like crystals resemble closely those observed in single crystals of nylon grown from various organic solvents. Fig 1(b) shows an electron diffraction pattern recorded from a single crystal crystallized upon cooling the PA4,6/water solution. It is apparent that the crystals shown in the TEM are single crystals of PA4,6 grown from the water solution. Similar observations hold good for a series of nylons.
Figure 2: Fig 1(a) shows a TEM image of lath-like single crystals grown from the water solution and (b) the corresponding electron diffraction pattern.

Figure 2: WAXD patterns of intensity versus reversed d-spacing are plotted for a 1:4 volume ratio of PA4,6 and water in a sealed glass capillary (heating/cooling rates used were 20°C/min), for (a) heating from 50°C to 230°C, (b) cooling back to 50°C, (c) second heating run to 260°C during which the capillary breaks at ~245°C and (d) cooling again to 50°C. (e) shows an overlay of the first frame in (a) and the last frame in (b), i.e. before and after dissolution of the PA4,6 in water.

References:
2. The influence of hydrogen bonding on the conformational changes, the Brill transition, and lamellae thickening in (co)polyamides; E Vinken, AE Terry, CE Koning, S Rastogi; Macromolecules 2006 (ma0526903) (in press)