Dissolution of Hydrogen-Bonded Polymers in Water: A Study of Nylon-4,6

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Introduction. The room temperature, ambient pressure crystalline structure of most nylons is formed from hydrogen-bonded β-sheets linked by weak van der Waals interactions. It is this hydrogen bonding that plays a prominent role in both the crystallization and melting behavior of these materials and also lends nylons their ubiquitous strength and intractability. However, Fourier transform infrared (FTIR) studies on nylon-10,10[1] 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[2] 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 pseudohexagonal phase, the (100) reflection related to the interchain/intrasheet distance merging into the (010)/(110) intersheet reflection at this temperature.[3−6] The Brill transition and melting temperatures in nylons show a strong dependence on the molecular structure and molecular weight: in nylon-4,6 the Brill transition occurs much below the melting temperature of ∼295 °C,[7] whereas in nylon-10,10 the transition occurs just below the melting temperature of 197 °C.[8,9] It should be noted, however, the crystallization conditions and the molecular weight can affect the Brill transition temperature and lead to some discrepancies between published temperatures, e.g., nylon-4,6 in the range 180−250 °C.[3,10] However, it can be supposed that since nylon-4,6 exhibits such a high Brill transition temperature compared to those of several other nylons, e.g., nylon-6 with a Brill transition temperature of ∼150 °C,[11] the hydrogen bonding is likely to be more affected at the Brill transition temperature in this polymer. 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 0.37 nm, respectively, only being achievable after annealing at elevated temperatures or upon solution crystallization.[10] Initially on cooling below the Brill transition, various authors[3,10,12] show that nylon-4,6 transforms into a high-temperature triclinic (monoclinic) phase in which the interchain and intersheet distances are closer together (0.41−0.42 and ∼0.40 nm, respectively), followed by a transition to a room temperature triclinic phase typical of other nylons.

Pressure is an important component that is present during the processing of polymers. While 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 22.10 MPa, the supercritical region in the $p-T$ water phase diagram is reached.[13] However, above the ambient boiling point and below the supercritical point, water is in the superheated state where the hydrogen bonding weakens considerably, and the water molecules are highly mobile.[14] Thus, in a polymer where hydrogen bonding exists, for example nylon-4,6, 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 1.25 MPa,[13] and therefore, complete dissolution can be achieved even at moderate pressures. In this communication we have explored the structural and conformational changes occurring in this dissolution process for the two-component system, nylon-4,6 and water, using time-resolved WAXD and FTIR.

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 1.5 mm and length 10 mm. The glass capillary was heated and cooled at 20 °C/min using a Linkam TMS600 hotstage. The changes occurring were followed in situ by means of WAXD at the Materials Science beamline (ID11) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. A 25 keV ($\lambda = 0.4966$ Å) X-ray beam of size 300 μm was used. Two-dimensional diffraction patterns were recorded every 20 s with a Bruker CCD detector for a 10 s exposure. The patterns were corrected for spatial distortion and integrated to give intensity against 2θ. A silicon standard (NIS 620b) was used to calibrate the exact sample-to-detector distance and Bragg d values for the various crystalline reflections. The results are shown plotted against reversed d-spacing, for clarity. A PA4,6 sample without water was also studied in order to confirm the Brill transition and melting temperatures.

By the above procedure it was possible to completely dissolve the PA4,6 in water at temperatures above 200 °C. Upon cooling the solution to 25 °C, a single crystal suspension was formed. A droplet of this suspension was placed on a carbon-coated copper TEM grid and allowed to dry naturally in a fume hood. The single crystals thus formed were analyzed using a Philips transmission electron microscope (TEM) without coating in metal.

The single crystals were also studied with FTIR. In this case, deuterium oxide (D_2O) was used as a solvent instead of water to avoid the overlap of the water bands and the PA4,6 bands. A droplet of the suspension of single crystals, formed upon cooling after dissolution in D_2O, was placed on a zinc selenium disk and then dried in a vacuum oven at 80 °C overnight. FTIR spectra, the average of 200 scans, were collected on a Bio-Rad FTS6000 spectrometer with a resolution of 2 cm^{-1}, after slowly cooling back to room temperature. Further room temperature spectra were collected between annealing

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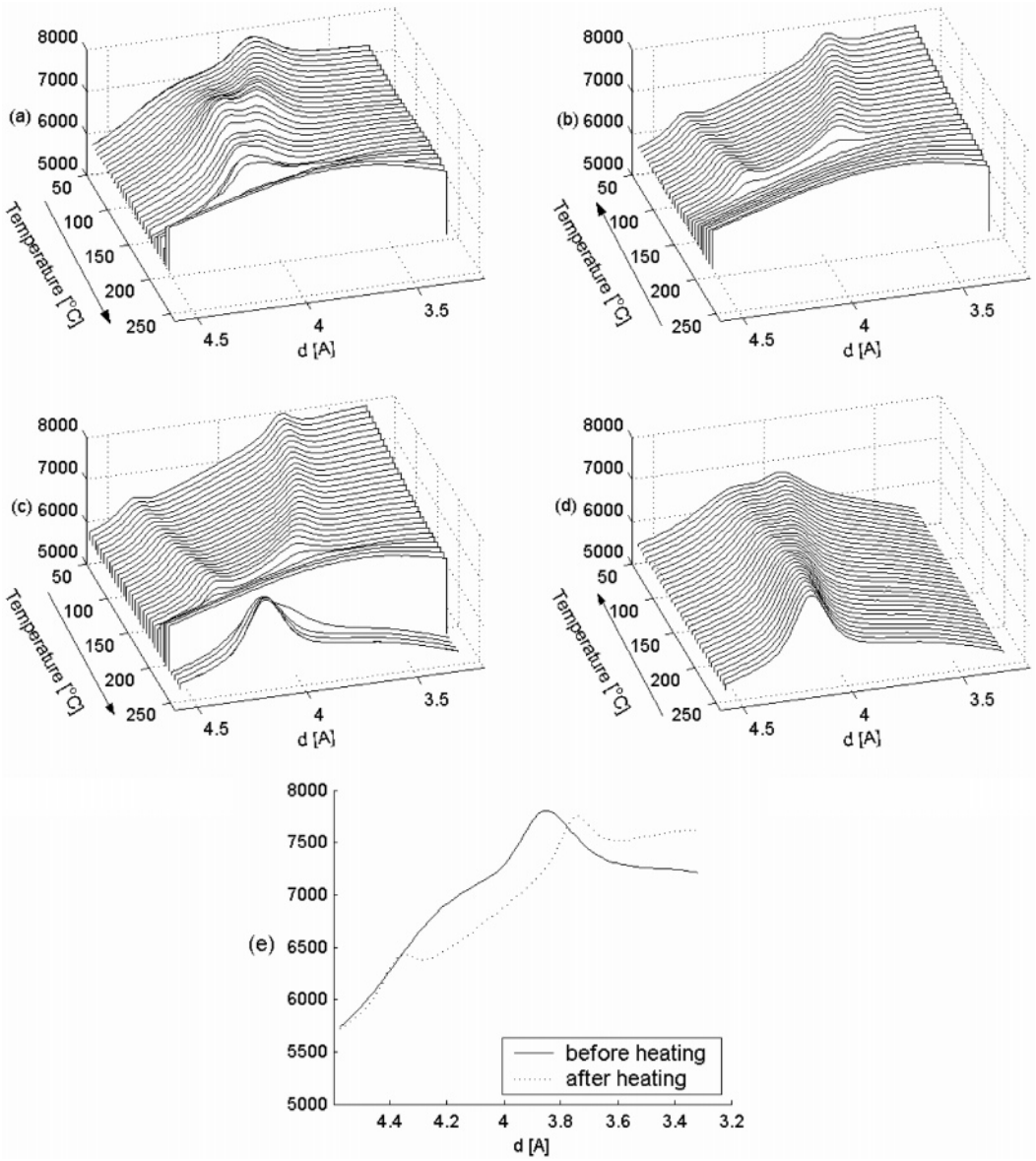

Figure 1. WAXD patterns of intensity vs reversed *d*-spacing are plotted for a 1:4 volume ratio of PA4,6 and water in a sealed glass capillary (heating/cooling rates used were 20 °C/min) for (a) heating from 50 to 230 °C, (b) cooling back to 50 °C, (c) second heating run to 260 °C during which the capillary 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.

the same sample at 150, 200, and 250 °C for 30 min at each temperature and allowing the sample to cool slowly to room temperature.

Results and Discussion. Figure 1 shows a series of WAXD patterns recorded during heating and cooling at 20 °C/min for PA4,6/H_2O in the volume ratio of 1:4 sealed in a 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,[2−8] 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 1a), a characteristic behavior of nylons.[2−5] Around 100 °C, the reflection associated with the interchain distance shows a sudden increase in intensity that may be due to reorganization/crystal perfecting. Since the encapsulated water in the capillary cannot escape, the water vapor pressure starts to build with increasing temperature.[13] 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 pseudohexagonal phase at the Brill transition temperature. On further heating, at ∼205 °C, the well-defined single reflection corresponding to the pseudohexagonal phase disappears with a corresponding small increase in the amorphous halo, suggesting the complete dissolution of PA4,6 in water. The initial, room temperature *d*-spacings of 0.42 and 0.39 nm for the interchain and intersheet distances, respectively, are very close to the high-temperature triclinic (monoclinic) phase identified in nylon-4,6.[3,10,12] It may be that the molecular weight or the fact that our sample was not annealed at high temperature leads to the appearance of this phase at room temperature. Indeed, the Brill transition in our sample of PA4,6 occurs at quite a low temperature within the range of the published values, from 180 to 250 °C,[3,10] perhaps a sign of the lack of crystal perfection and differences in the crystallite size within our nascent material. We have confirmed the interchain and inter-

sheet distances by WAXD for a dry sample of PA4,6 without water heated at 20 °C/min within the Linkam, although the Brill transition did occur at a slightly higher temperature (~215 °C).

Upon cooling the PA4,6/H_2O solution from the maximum temperature of 230 °C, Figure 1b 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 pseudohexagonal phase in contrast to recrystallization 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 1a, with the final pattern following complete dissolution from Figure 1b, it is still apparent that the interchain distance (0.44 nm) in the PA4,6 crystallized from the water solution is at a higher d value compared to that of the PA4,6 before heating and the intersheet distance is contracted (0.37 nm). This is shown more clearly in Figure 1e for the diffraction patterns at 50 °C. The recrystallization 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 also to point out that GPC results (not shown) confirm that the dissolution process did not change the molecular weight of PA4,6.

Figure 1c shows WAXD patterns recorded during the consecutive heating of this solution of PA4,6/H_2O 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 Figure 1a,b. The Brill transition must be at a higher temperature than for the initial run because the pseudohexagonal 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 3.65 MPa,[13] 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[8]), crystallizes directly into the pseudohexagonal phase. Therefore, the Brill transition for the water solution crystallized sample must be between 205 and 245 °C. The last three frames heating to a maximum temperature of 260 °C in Figure 1c shows the crystallization of PA4,6 in the pseudohexagonal phase. It is to be noted that the single broad reflection at 0.42 nm of the pseudohexagonal phase just after the Brill transition typically increases in intensity and becomes sharper with time.

Figure 1d 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 pseudohexagonal phase transforms into the triclinic phase. Because of the low Brill transition temperature, we can conclude that the recrystallization upon evaporation is highly disordered despite possible brief annealing at high temperatures, and indeed the final interchain and intersheet distances are 0.42 and 0.40 nm, respectively; i.e., the PA4,6 has recrystallized in the high-temperature triclinic phase.

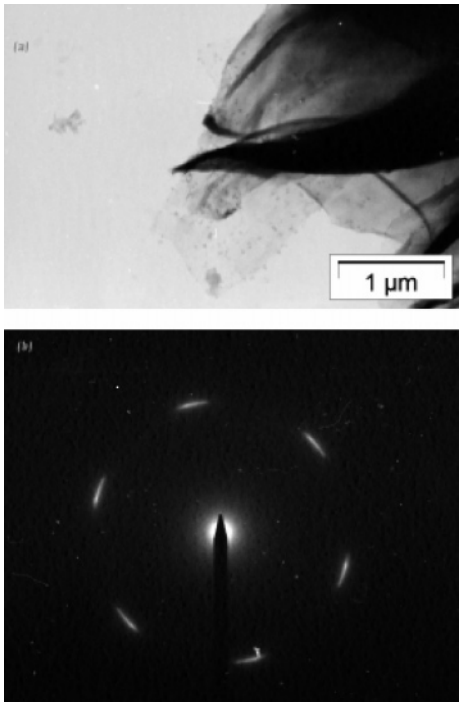

Figure 2. (a) shows a TEM image of lathlike single crystals grown from the water solution and (b) the corresponding electron diffraction pattern.

From the series of X-ray diffraction patterns reported in Figure 1, it is evident that PA4,6 dissolves in water just above 200 °C. It is also possible to recrystallize the PA4,6 from this water solution. Figure 2a shows a typical transmission electron micrograph of the PA4,6 crystals grown by the above process. The lathlike crystals resemble closely those observed in single crystals of nylon grown from various organic solvents.[15] Figure 2b shows an electron diffraction pattern recorded from a single crystal crystallized upon cooling the PA4,6/water solution. A 6-fold symmetry is apparent but possibly arises due to the preferential orientation of the single crystals, as has been seen previously by Atkins et al.;[15] tilting of the crystal would bring up information from the other crystalline planes. Despite this, it is apparent that the crystals shown in the TEM are single crystals of PA4,6 grown from the water solution. The detailed crystal structure is under investigation. However, we were intrigued as to whether water was actually being intercalated within the PA4,6 crystalline lattice. To follow this and the conformational changes, FTIR studies were performed on PA4,6 crystals grown from D_2O, as stated earlier D_2O being chosen to avoid the overlap of the water bands with the PA4,6 bands. WAXD was used to confirm that there was no change in the dissolution process for PA4,6 upon replacing H_2O with D_2O.

Figure 3a shows room temperature FTIR spectra of PA4,6, D_2O, and PA4,6/D_2O crystals (grown from the PA4,6 and D_2O solution and dried at 80 °C). No vibrational bands in the region of 2300−2600 cm^{-1} in the nonsolvated PA4,6 are observed. The spectra of only D_2O shows a broad band at 2507 cm^{-1};[16] however, the

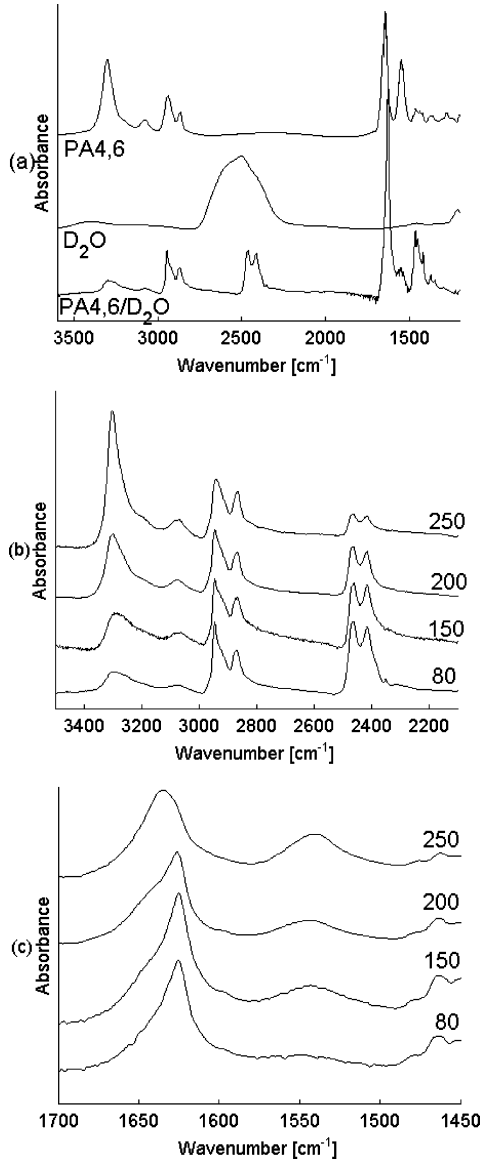

Figure 3. (a) FTIR spectra of PA4,6, D_2O liquid, and PA4,6/D_2O crystals. (b) and (c) show two expanded portions of each room temperature FTIR spectrum for the same sample annealed at 150, 200, and 250 °C. All the spectra have been normalized relative to the intensity of the methylene (CH_2) groups centered at 2900 cm^{-1}.

PA4,6/D_2O crystal does not show this broad band. Instead, it shows a narrower band consisting of two peaks at 2460 and 2415 cm^{-1}, which we suggest is due to the binding of the D_2O between the carbonyl (C═O, amide I) and N−H groups of adjacent nylon chains. Simultaneously with the appearance of these D_2O vibrations, a considerable decrease and flattening in the intensity of the H-bonded N−H stretch at ∼3300 cm^{-1} is observed with no appearance of the free N−H stretch at 3440 cm^{-1}. It is to be noted that although the crystals have been dried in a vacuum oven at 80 °C, D_2O is still retained in the crystal lattice.

The PA4,6/D_2O crystals were then annealed for 30 min at different temperatures: 150, 200, and 250 °C. After annealing, the crystals were slowly cooled back to room temperature and the FTIR spectra recorded. Figure 3b shows the changes in the 3500−2100 cm^{-1} region of the IR spectra and Figure 3c the 1700 and 1450 cm^{-1} range. The bands centered on 2415 cm^{-1}, associated with the D_2O, decrease in intensity, suggesting that the bound D_2O can now leave the crystalline lattice, as the temperature nears the Brill transition, which we know from Figure 1c to be between 205 and 245 °C. In the same spectra the bands at 3300 and 1541 cm^{-1}, assigned to the N−H stretch and the in-plane N−H (amide II) deformations, respectively,[17] show an increase in intensity. At the same time, the peak due to the carbonyl groups (amide I) also shifts to higher wavenumbers from 1625 to 1635 cm^{-1}, suggesting an increase in the vibrational motion. In totality, these experimental findings clearly demonstrate that once the D_2O molecules bound to the crystalline lattice leave, the amide groups become more mobile. These observations with our X-ray data reveal an intercalation of water within the nylon crystalline lattice.

Conclusions. The study reported in this communication conclusively demonstrates that a hydrogen-bonded polymer, in this case PA4,6, is soluble in water much below the supercritical temperature of water. Superheated water as a solvent facilitates the growth of single crystals and provides a novel route to form water intercalated highly crystalline single crystals, where the values of the interchain and intersheet distances are close to ideal. The bound water molecules exit from the lattice around the Brill transition temperature of PA4,6, upon the release of vapor pressure. These observations open a novel ecofriendly route for water dissolution of hydrogen-bonded materials in general, independent of whether they are synthetic in nature or biopolymers, thus providing new opportunities for coating technology and nanocomposites.

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