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New Crystalline Transitions in Nylons 4,6, 6,10, and 6,12 Using High Temperature X-ray Diffraction Studies

C. Ramesh

Polymer Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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ABSTRACT: The crystallization of nylons 6, 10, 6,12, and 4,6 was monitored in situ by X-ray diffraction from the melt. Nylons 6,10 and 6,12 were found to crystallize into the α-phase as indicated by the two-peak nature of the diffractogram. Nylon 4,6 crystallized with a single peak, which is characteristic of the γ-phase (hexagonal structure). On cooling from the crystallization temperature to room temperature, nylons 6,10 and 6,12 preserved the two-peak nature; however, detailed data analyses indicated a change from the high-temperature (HT) α-phase to the low-temperature α-phase (triclinic structure) below 200 °C. Amorphous nylons 6,10 and 6,12 crystallize in the hexagonal structure when heated from room temperature (RT) and transform into the HT α-phase above 190 °C. But if cooled before this transition, these samples exhibit γ-phase to α-phase transitions (Brill transitions). Nylon 4,6 crystallized from the melt in the γ-phase, transformed into the HT α-phase about 40 °C below the crystallization temperature and showed a further transition ∼150 °C below the crystallization temperature. The second transition is from the HT α-phase to the RT α-phase.

Introduction

The nylons are important semicrystalline polymers with many useful properties. Among nylons, nylon 6,6 and nylon 6 are commercially successful and have been extensively explored scientifically, while nylons 6,10 and 6,12 have received less attention. Nylon 6,6 shows a crystal to crystal transition on heating, known as the Brill transition.[1] The room temperature triclinic structure transforms into a pseudohexagonal structure at elevated temperatures. The Brill transition is most clearly displayed in X-ray diffraction studies, as the two prime strong reflections of nylon 6,6, the 100 and 010/110, merge into a single reflection at the transition. The Brill transition in nylon 6,6 has been the most extensively studied.[1−7] These transitions have been reported for many other even−even nylons.[8−10] In the case of nylon 6,6, it has been shown that Brill temperature strongly depends on the crystallization temperature.[2] Unlike nylon 6,6, which can exist as a stable modification below the crystallization temperature (T_C),[2] nylon 6,12 has been reported to crystallize on pseudohexagonal structure[8] and transforms into the triclinic structure immediately below T_C on subsequent cooling. Brill transitions on heating solution grown single crystals of nylon 6,10 and nylon 6,12 have been shown to coincide with the melting temperature.[9] The nylons 2,6, 2,12, and 4,4 also exhibit Brill transition behavior similar to nylon 6,6.[10] In general the Brill transition is a feature of even−even nylons on heating. However, Murthy et al., have observed that the room-temperature (RT) monoclinic structure of nylon 6 transforms into a high-temperature (HT) monoclinic structure on heating nylon 6 from RT and considered this a Brill transition.[7]

Hydrogen bonding dominates the crystal structure of nylons; hydrogen-bonded sheets are the main feature of the nylon structure and the two strong reflections arise from this feature. The *d* spacings of these reflections at 0.37 and 0.44 nm are due to the intersheet distance between the sheets and the projected interchain distance within the sheet, respectively. The structure is called the α-phase if the hydrogen-bonded sheets are sheared and stacked progressively, while the β-phase results if it is in alternating shear. The room-temperature crystal structure of nylons 6,6,[11] 6,10, and 6,12[12] is triclinic and toward the α-phase. The α-phase of nylon 6 has a monoclinic structure[13] and the hydrogen-bonded sheets are in alternating shear. The structure of solution-grown nylon 4,6 single-crystal mats[14] is like the nylon 6 α-phase, rather than like the nylon 6,6 α-phase. The high-temperature pseudohexagonal structure, which is also known as the Brill structure, is called the γ-phase. The characteristic of the γ-phase is that it exhibits only one strong reflection and the *d* spacing is 0.42 nm. We designate, collectively, the structures that exhibit two distinct peaks in the X-ray diffractogram as α-phases in the case of nylons 4,6, 6,10, and 6,12 and structures that show only one peak as the γ-phase, hexagonal phase, or Brill structure. Also we term the crystalline transition as the Brill transition when the transition is from the α-phase to the γ-phase on heating or from the γ-phase to the α-phase on cooling.

The Brill transition in nylons has been attributed to the anisotropic thermal expansion.[3,15] The hydrogen-bonded sheets start expanding and thus increase the *d* spacing with an increase in temperature. The *d* spacing of 100 planes does not change because the planes are anchored by the hydrogen bonds. At the Brill temperature, both spacings become equal and the hydrogen bond can flip 60° out of sheet and form intersheet hydrogen bonds. This leads to a three-dimensional network of hydrogen bonds above the Brill temperature. However, this aspect has been questioned on the basis of high-temperature structure analysis,[3] H NMR studies,[6] and other physical properties such as birefringence.[2]

Most of the existing studies[1,3−11] that deal with the Brill transition have been made on heating precrystallized samples and look at the transition on heating from room temperature. In the present paper we report the results of a study on the crystallization of nylons 4,6, 6,10, and 6,12 at high temperature, from the melt state,

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and the crystalline transitions on cooling from the crystallization temperature and then on heating from room temperature (RT) to melting using a hot stage attached to an X-ray diffractometer. These nylons show the Brill transition and other crystalline transitions which have not been reported so far.

Experimental Section

The samples of nylons 6,10, 6,12, and 4,6 were obtained from Aldrich. The X-ray diffraction experiments were performed using a Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator and wide angle powder goniometer fitted with a high-temperature attachment. The generator was operated at 40 kV and 125 mA. The sample holder was a copper block, and a thin film of the sample was formed on that block by melt pressing the sample. Initially the sample was heated in the X-ray hot stage well above the melting temperature of the sample to remove the melt memory effects and then cooled to the crystallization temperature. It was cooled/heated at the rate of 20 °C/min and when the sample temperature reached a point within 20 °C of the required set temperature the cooling/heating rate was automatically reduced to 2 °C/min to minimize the overshooting of the set temperature. The temperature was maintained within 1 °C of the set temperature thereafter. The maximum temperature that can be reached in the hot stage is 300 °C.

In situ crystallization studies had been made only at temperatures close to melting temperature because at these temperatures the crystallization rate of nylons was low and the sample was still in amorphous state after cooling from the melt. The crystallization temperature (T_C) was 210 °C for nylons 6,10 and 6,12. Nylon 4,6 was crystallized at 280 °C.

The development of the crystalline structure during the isothermal crystallization process was studied by scanning the sample at regular time intervals. After the crystallization was completed, the sample was cooled to room temperature and the change in the crystal structure was monitored by scanning at different temperatures during cooling. The sample was again heated to melting, and the change in the crystal structure was monitored by scanning at different temperatures until the melting was completed.

It is apparent from the X-ray diffraction patterns that in the transition regime the position of the peaks can only be fixed by deconvoluting the peaks. The method followed has been described elsewhere.[2]

Results

Nylons 6,10 and 6,12. The course of the isothermal crystallization of nylon 6,10 at 210 °C as followed by X-ray diffraction is shown in Figure 1a. The crystalline peaks develop slowly with time, because the super cooling is very low. It can be seen from the figure that during isothermal crystallization at 210 °C, the pattern shows a sharp peak at $2\theta = 20.80°$ with a shoulder. The deconvolution of the X-ray pattern shows that the pattern consists of two crystalline peaks and one amorphous peak. The shoulder is due to a crystalline peak at $2\theta = 21.24°$. The *d* spacings corresponding to these two crystalline peaks are 0.429 ± 0.001 nm and 0.415 ± 0.001 nm, respectively, and are different from the *d* spacing of the hexagonal structure, which is 0.42 nm. The two-peak nature of the diffractogram indicates that the sample has crystallized in the α-phase.

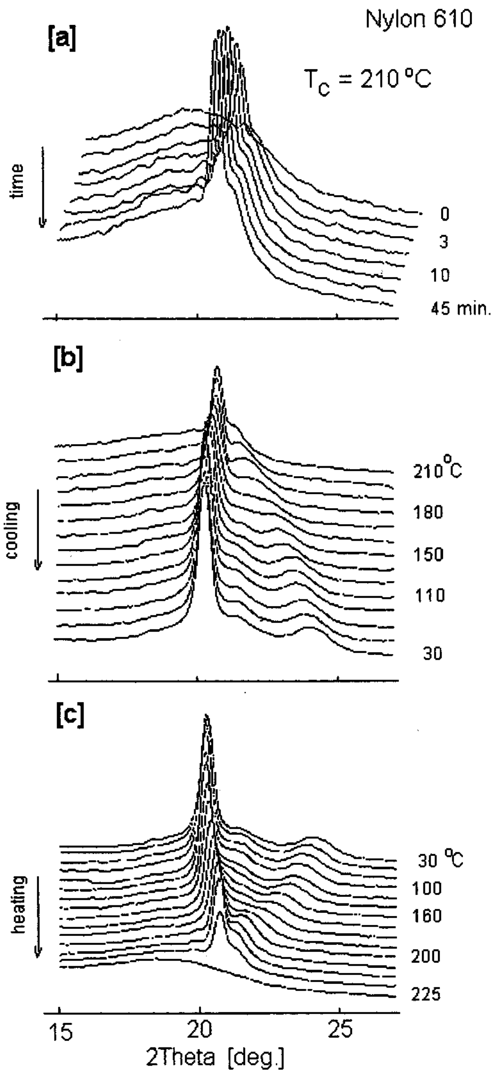

Figure 1. X-ray diffraction pattern obtained during (a) the isothermal crystallization of nylon 6,10 at 210 °C, (b) cooling from 210 °C, and (c) heating from room temperature to melting.

On cooling from the crystallization temperature, the minor peak at $2\theta = 21.24°$ starts moving away from the sharper peak, while the sharper peak at $2\theta = 20.80°$ shows a small shift toward lower angle as shown in Figure 1b. On cooling from T_C, at some stage a new peak at $2\theta = 21.715°$ appears between the two peaks already present but close to the strong peak at $2\theta = 20.80°$. The variation in *d* spacing with cooling temperature for these three peaks is shown in Figure 2a. The *d* spacing due to the sharper peak (0.429 nm) shows a small but noticeable increase in the temperature range 170−200 °C, while cooling from 210 °C to room temperature. In this temperature range, the spacing due to the smaller peak also shows a higher rate of decrease. Such a behavior is indicative of a crystalline transition. Nylons 6,6,[2] 2,6, and 4,4[10] also show some similarity in the behavior of the *d* spacings in the Brill transition temperature zone. In nylons 6,6,[2] 4,4, and 2,6,[10] the transition is from the hexagonal structure to the triclinic structure or vice versa, depending on whether it is observed during cooling or heating, respectively. However, in the present case, for nylon 6,10, the crystalline transition is from an α-phase, which is formed at the crystallization temperature to another α-phase which is stable at low temperatures. The room-temperature crystalline structure of nylon 6,10[12] is triclinic. Below the transition temperature, the *d*-spacing variation is similar to the *d*-spacing variation of nylon 6,6. The variations in diffraction pattern and *d* spacings on cooling from T_C are found to be reversible on heating the sample from RT to melting and are shown in Figures 1c and 2b, respectively. It is seen from the figures that

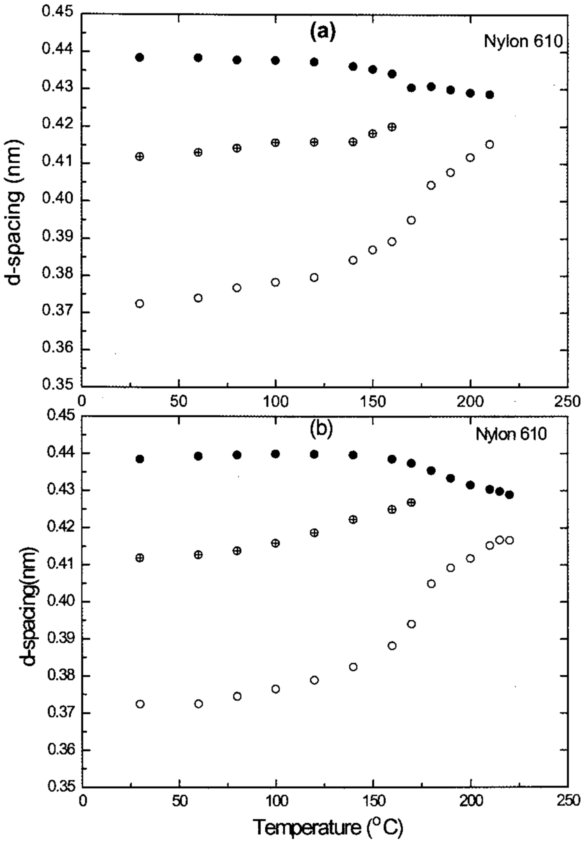

Figure 2. Change in *d* spacing for nylon 6,10 with temperature during (a) cooling from 210 °C to RT and (b) heating from RT to melting.

the high-temperature α-phase is preserved until melting.

The nylon 6,10 sample that is quenched rapidly to room temperature from the melt does not crystallize but remains in the amorphous state. This is seen from the amorphous diffraction pattern at room temperature (first curve in Figure 3a). When the amorphous sample is heated, the broad amorphous peak becomes progressively sharper with increasing temperature, indicating crystallization. The single sharp peak and the *d* spacing at 0.415 nm indicate that the sample crystallized in the hexagonal structure. However, when the sample is heated above 190 °C, a second peak appears as a shoulder to the main peak, indicating that the transition of the hexagonal structure into the high-temperature α-phase has taken place. The α-phase is preserved until melting at 225 °C. The variation of the *d* spacing of this sample with temperature is shown in Figure 4a.

The behavior of the sample is different, however, if it is not allowed to melt but held at temperatures below the γ-phase to α-phase transition and then cooled to room temperature. The diffractograms obtained on cooling from the holding temperature 180 °C show that the hexagonal structure transforms into triclinic structure, by the appearance of a second peak corresponding to the 010/110 reflection, indicating a Brill transition (Figure 3b). This peak appears about 30 °C below the holding temperature. A similar behavior is obtained for holding temperatures (T_c) at 130, 160, and 190 °C. Table 1 shows the holding and the corresponding transition temperature. The Brill temperature is always lower than the holding temperature and $T_c - T_B$ is approximately constant by 30 °C. However, for the holding temperature 200 °C, the structure has already been transformed into a high-temperature α-phase from the low-temperature hexagonal structure and on cooling the high-temperature α-phase transforms into a low-temperature triclinic structure. These results can be seen in Figure 4b, which shows the *d* spacing as a function of cooling temperature for samples cooled to room temperature from various holding temperatures.

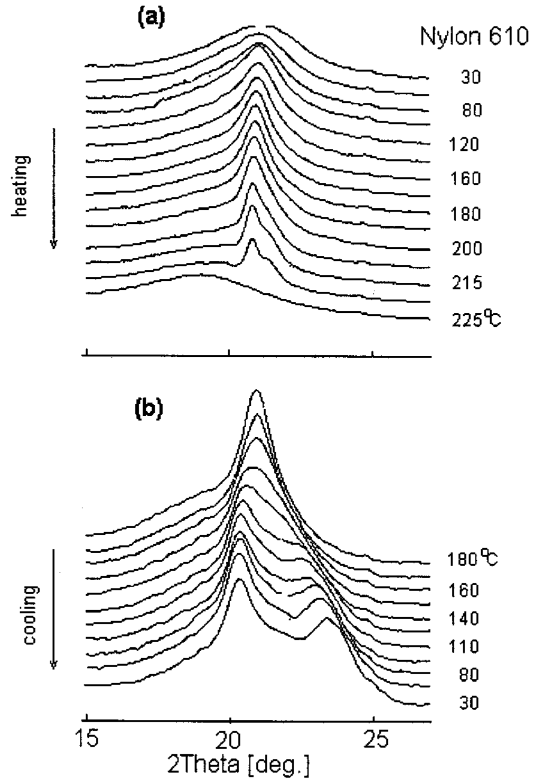

Figure 3. Behavior of the X-ray patterns: (a) quenched amorphous nylon 6,10 on heating from RT to melting and (b) the X-ray diffraction patterns obtained on cooling from holding temperature 180 °C.

The data on a similar study with nylon 6,12 will not be presented here in detail as nylon 6,12 shows similarity with nylon 6,10 behavior on crystallization and subsequent cooling and heating. Very briefly, nylon 6,12 crystallizes at 210 °C in high temperature α-phase and on subsequent cooling transforms into the RT α-phase. Nylon 6,12 when heated from the amorphous state crystallizes into hexagonal structure and transforms into a high-temperature α-phase at about 190 °C. If the sample is cooled to room temperature before the appearance of the second peak above 190 °C, the sharp single peak splits into two peaks. Unlike nylon 6,10 in which the splitting occurs about 30 °C below the holding temperature, for nylon 6,12 it occurs within 10 °C below the holding temperature.

In nylons 6,10 and 6,12 the small peak at $2\theta = 21.715°$ indicates the presence of a small amount of material in a hexagonal structure while cooling from T_C. This phase is evident only after the HT α-phase to RT α-phase transition on cooling. At this stage the exact origin of this phase is difficult to identify; nevertheless it can be speculated that the hexagonal phase also crystallizes along with the HT α-phase at the crystallization temperature, but cannot be identified because it is masked by the two peaks of the HT α-phase. Jones[9] et al. also report the existence of the hexagonal phase along with triclinic phase at room temperature in

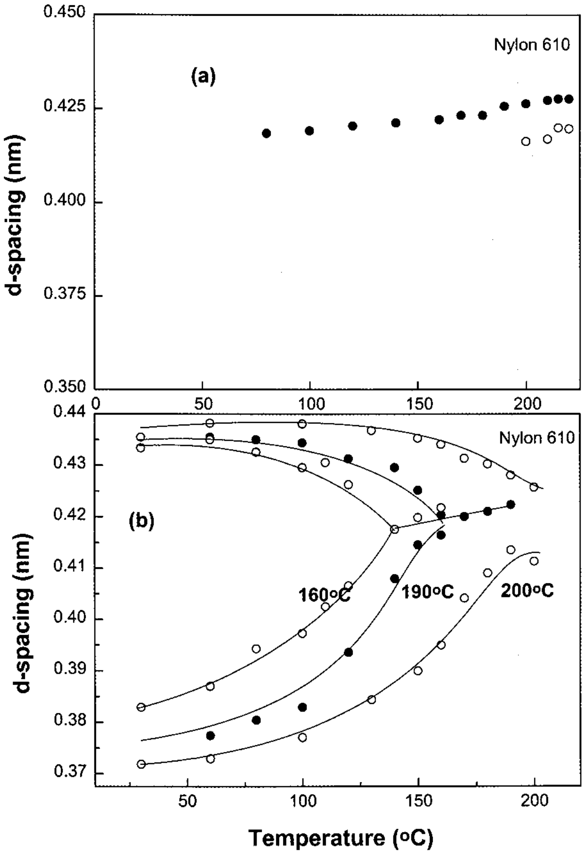

Figure 4. Variation of *d* spacing of (a) a quenched amorphous nylon 6,10 sample on heating and (b) the variation of *d* spacing during cooling from various holding temperature.

Table 1. Crystallization/Holding Temperature (T_C) and Brill Temperature (T_B) of Nylon 6,10

T_C, °C	T_B, °C	$T_C - T_B$, °C
130	100	30
160	140	20
180	150	30
190	160	30

solution grown single crystal mats of nylons 6,10 and 6,12 and that the hexagonal phase disappears only at the melting temperature.

Nylon 4,6. The course of isothermal crystallization of nylon 4,6 at 280 °C is shown in Figure 5a. The appearance of a small crystalline peak even at the first scan is due to the presence of a small portion of the crystalline material which does not melt at 300 °C, the highest temperature that could be reached in the X-ray hot stage. The crystalline peak grows in intensity slowly with time indicating crystallization. The single sharp peak at $2\theta = 21.23°$ indicates that during isothermal crystallization the sample crystallized in the hexagonal structure, unlike nylons 6,10 and 6,12 which crystallize in the α-phase. This sample shows the Brill transition on cooling from T_C, as recorded by the splitting of the single peak into two (Figure 5b). Similar to that for nylon 6,6,[2] the Brill transition occurs at temperatures considerably lower than the crystallization temperature. The behavior of the two peaks on cooling from the Brill temperature is far more complicated than the behavior exhibited by nylon 6,6 or the other two nylons discussed here. This is more clearly seen from Figure 6a, in which the *d* spacing is shown as a function of temperature. After the transition into the α-phase from a hexagonal structure, the two prominent reflections do not move away rapidly from each other on further cooling as in the case with nylon 6,6 or 6,10 but remain close. However, on reaching a temperature around 120 °C, the spacing due to the projected interchain distance (100 reflection in the case of triclinic structure and indexed as 200 for the monoclinic structure) increases rapidly on further cooling, and at room temperature, it reaches the conventional value of 0.433 nm. On the other hand the spacing of the other reflection (010/110 reflections in the case of triclinic structure and indexed as 202/002 reflections for monoclinic structure) continues to decrease in a linear fashion to 0.377 nm (inter sheet distance) at room temperature. This indicates a second crystalline transition for nylon 4,6, which is from the HT α-phase to another RT α-phase at a temperature close to 120 °C. The transitions and variations in *d* spacings are reversible on heating from RT to melting. The diffractograms and *d* spacings on heating are shown in Figures 5c and 6b, respectively.

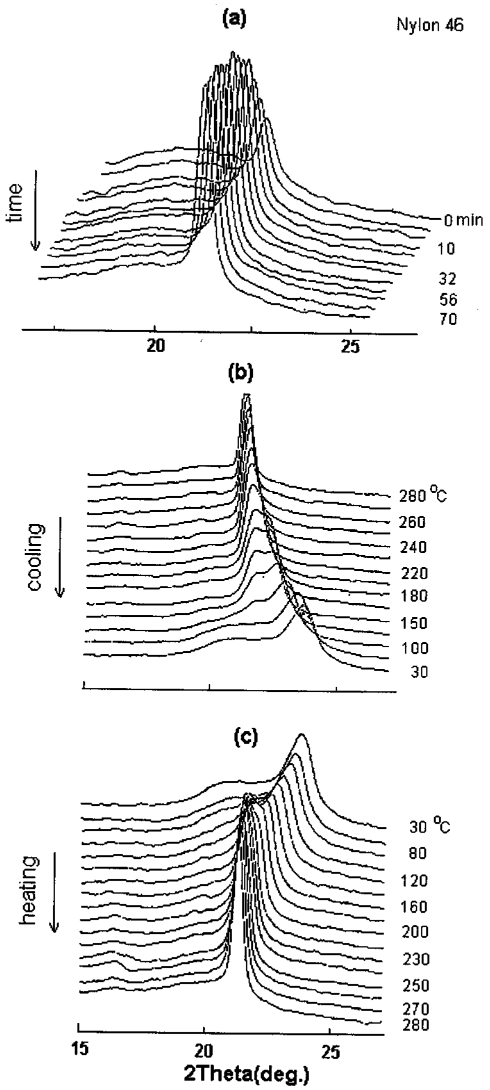

Figure 5. X-ray diffraction pattarn of nylon 4,6 during (a) isothermal crystallization at 280 °C, (b) cooling to room temperature, and (c) heating from RT to melting.

The cooling rate of the hot stage is too limiting to study the crystallization behavior of the samples below 280 °C as the sample crystallizes very rapidly before reaching the intended crystallization temperature. Al-

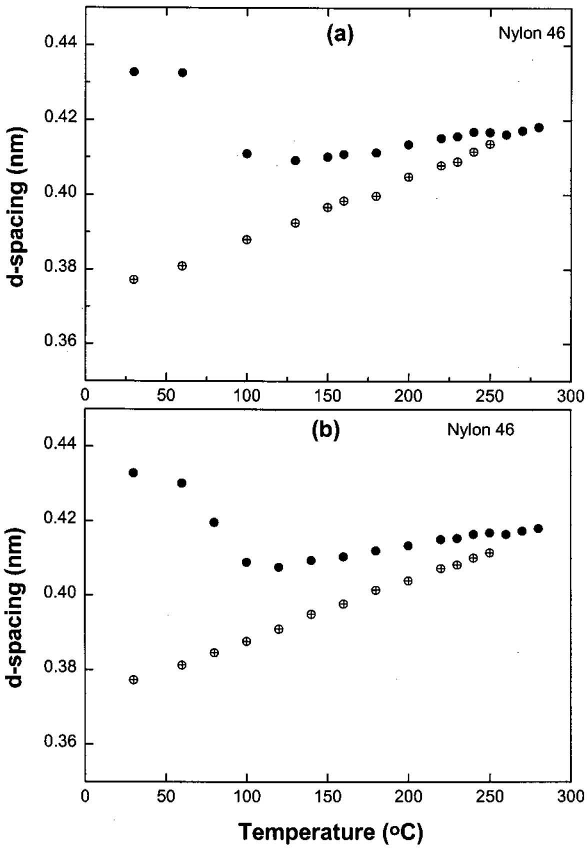

Figure 6. Change in *d* spacing with temperature for nylon 4,6 during (a) cooling from T_c to RT and (b) heating to melting from RT.

Table 2. Crystallization/Holding Temperature (T_C), Brill Transition Temperature (T_B) and Low-Temperature (T_L) Transition of Nylon 4,6

T_C, °C	T_L, °C	T_B, °C	$T_C - T_L$, °C	$T_C - T_B$, °C
220	80	180	140	40
240	100	200	140	40
260	110	220	150	40
280	120	250	160	30

ternatively, a rapidly quenched sample is annealed at 220, 240, and 260 °C for about 30 min and then cooled to room temperature to study the effect of holding temperature on the Brill transition. The behavior of the diffraction pattern and *d* spacings are similar to the sample crystallized at 280 °C on cooling. However, the Brill transition and the low-temperature crystalline transition are shifted to lower temperatures. Table 2 shows the annealing temperature and the corresponding Brill temperature and the low-temperature transition (T_L) for various holding temperatures.

Discussion

The key observation made in this work is the crystallization of nylons 6,10 and 6,12 directly into an α-phase when crystallized from the melt above 200 °C and their subsequent transition into room-temperature triclinic structures on cooling. Though the X-ray data is not sufficient to calculate the exact nature of the structure, it is assumed that this high-temperature α-phase structure is similar to the room-temperature triclinic structure. It has been shown that the room-temperature structure of nylon 6,10[12] is similar to the nylon 6,6 triclinic structure but with an appropriately longer *c*-axis. A detailed structure determination has not been performed for nylon 6,12, but X-ray diffraction data obtained from single-crystal mat is consistent with the triclinic unit cell.[12] The crystalline transition is not very obvious in the diffraction patterns (parts b and c of Figure 1), but careful analysis of the data reveals the transition. The transition is discernible in both the cooling and the heating cycles. Murthy et al.,[7] have shown that for nylon 6 the structure transforms from a room-temperature monoclinic to a high-temperature monoclinic structure on heating. The crystallization of nylon 6,10 and 6,12 directly into a triclinic structure differs from nylon 6,6,[2] which always crystallizes into a hexagonal structure when crystallized from the melt and then transforms into a triclinic structure on cooling. The solution-grown single crystals of nylons 6,10 and 6,12 behave slightly differently from melt crystallized samples reported here. Jones[9] et al., found that when the single-crystal mats of nylons 6,10 and 6,12 are heated from room temperature to melting, the two strong diffraction signals of 0.44 and 0.37 nm *d* spacings move close to each other and become a single spacing at the melting temperature, indicating that the Brill temperature is coincident with the melting temperature.

The present data indicate that the crystallization and subsequent transition behavior of nylons 6,10 and 6,12 are temperature dependent. The temperature range from RT to melting can be divided into two regimes. For the range above 190 °C (high-temperature regime), these nylons always exist in the HT triclinic structure and transform into the RT triclinic phase on cooling to below 200 °C. However, if they are crystallized below 200 °C (low-temperature regime), these nylons crystallize into a hexagonal phase and show a Brill transition into a triclinic structure on cooling, and the behavior is similar to the well established behavior of nylon 6,6. It could be said that nylon 6,6 has only a low-temperature range and melts before reaching the second regime in which it can exist in the HT triclinic form.

The *d* spacing behavior of nylon 4,6 with temperature is more complicated when compared to nylon 6,6 and other nylons discussed here and shows unusual behavior of *d* spacings in relation with temperature. Hill and Atkins[16] report a plateau region in the *d* spacing when nylon 4,6 single-crystal mats are heated above room temperature. Though no explanations can be offered at this stage for the strange behavior of *d* spacings with temperature, it must be noted that the solution-grown crystals of nylon 4,6 incorporate an amide group in the fold and can hydrogen bond among successive hydrogen-bonded sheets.[14]

Nylons 6,10, 6,12, and 6,6 have similar structure and fold schemes but different hydrogen bond densities. The possible reason for the differences shown by these three nylons could be the influence of the methylene segmental motion between the hydrogen bonds during heating. It has been shown by Murthy[7] et al. that at high temperatures the methylene segments are in motion but hydrogen bonds hold them in the sheet. They have also shown by NMR studies that for nylon 6 a small fraction of trans conformation in the crystals turn into the gauche conformation at high temperatures. The methylene segmental motion in the diacid segment will be different for these nylons. Nylon 6,12 will have the highest segmental mobility followed by nylons 6,10 and 6,6. This variation in the methylene group segmental motion could bring about the variation in the behavior of crystalline transitions shown by these nylons.

Conclusions

The in situ X-ray diffraction studies on the crystallization of nylons 6,10, 6,12, and 4,6 provide new information on crystalline transitions on cooling and heating. Some of the crystalline transitions are reported here for the first time. Nylons 6,10 and 6,12 crystallize directly into triclinic structures if crystallized from the melt in a narrow temperature range between 200 °C and melting temperature. This structure transforms into RT triclinic structure on cooling, and this transition is independent of crystallization temperature. However, these nylons crystallize into hexagonal structures similar to nylon 6,6 if they are crystallized at 190 °C or lower and show a typical Brill transition on cooling.

Nylon 4,6 shows two crystalline transition on cooling from the crystallization temperature. The first transition is about 40 °C below the crystallization temperature and is a typical Brill transition. The second one is about 140−150 °C below the crystallization temperature and is from the HT α-phase to the RT α-phase.

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