High-Temperature X-ray Diffraction Studies on the Crystalline Transitions in the α- and γ-Forms of Nylon-6

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ABSTRACT: The crystallization of nylon-6 from the melt was monitored in situ by X-ray diffraction. The nylon-6 was found to crystallize into a high-temperature α′-phase as indicated by the two-peak nature of the diffractogram. On cooling from the crystallization temperature to room temperature, nylon-6 retained the two-peak nature. However, data analysis indicates a change from high-temperature (HT) α′-phase to low-temperature α-phase at ∼180 °C. On heating, the α-phase transformed into the α′-phase at about 190 °C and melted in the α′-phase. The transition took place over a temperature range where both phases coexisted. However, samples crystallized from the melt at temperatures 140 and 180 °C showed the α-phase at room temperature, but on heating the α-phase first transformed into a pseudohexagonal phase and before melting the pseudohexagonal phase further transformed into the α′-phase. The α-phase was transformed into the γ-phase, by potassium iodide−iodine treatment, and the behavior of the γ-phase with temperature had been studied for the first time. The γ-phase was very stable and did not show any crystalline transition below the melting point.

Introduction

Nylon-6 is commercially important and one of the prominent members of the polyamide class of semicrystalline polymers. The structure and morphology of nylon-6 have been very extensively studied. Nylon-6 exhibits two crystalline modifications, namely the α-phase[1] and the γ-phase.[2] The α-phase has monoclinic structure, and the hydrogen bonds are formed between antiparallel chains. The γ-phase also has a monoclinic structure, but the twisted chains allow hydrogen bonds to be formed between parallel chains.[2] The α-phase is most commonly observed at room temperature and can be transformed into the γ-phase by treating in aqueous potassium iodide−iodine solution.[2−5] High-speed spinning also yields the γ-phase.[5] In nylon-6 fibers both phases can coexist, and the content of the phases depends on the spinning and drawing conditions.[6] The γ-phase is stable and may be converted into the α-phase by melting and recrystallization. Aharoni[7] sketches a scheme for the transformation of the α-phase into the γ-phase without local melting and crystallization. A third phase has also been reported by Stepanaik et al.,[3] Sandeman and Keller,[8] Tsuruta et al.,[9] Ziabicki,[10] and Rolden and Kaufman[11] which can be converted into the α-phase by annealing. Nevertheless, it has been suggested[6,12,13] that there exist only two basic structures, the α- and γ-phases. The crystal structure[1] of nylon-6 at room temperature is monoclinic, and the hydrogen-bonded sheets are sheared alternatively to form the α-phase. The characteristic peaks of the α-phase of nylon-6 at room temperature are at $2\theta = 21°$ and 24° and are indexed as 200 and 002/202 reflections, respectively. In the γ-phase, these peaks are indexed as 001 and 200/$\bar{2}$01 and appear at 22° and 23°, respectively. Also, the 200/$\bar{2}$01 reflections appear as a shoulder to the 001 reflection. Another observation is that the 020 reflection is weak in the α-phase, while as it is intense in the γ-phase.

The important feature of nylons is that the structure undergoes a crystalline transition when subjected to heating. The crystalline transition in nylon-6,6 has been well documented and is known as Brill transition.[14] In nylon-6,6, the RT α-phase transforms into a pseudohexagonal structure on heating. A crystalline transition is also reported for nylons-4,6,[15] -6,10,[15] and -6,12.[15,16] Murthy et al.[17] have observed that the room temperature (RT) monoclinic structure of nylon-6 transforms into a high-temperature (HT) monoclinic structure on heating from RT and considered it as Brill transition. The changes observed in the infrared spectra of nylon-6 and -6,6 during heating have been correlated to the Brill transition.[18] Nylon-12 crystallizes[19] into the α-phase on crystallization from the melt and transforms into the γ-phase on subsequent cooling to room temperature. We designate all the structures that exhibit two distinct peaks having *d*-spacing at 0.37 and 0.44 nm as α-phases. The structures that show two close but distinct peaks with *d*-spacing having values other than 0.37 and 0.44 nm are designated as α′-phase, which is different from the room temperature α-phase. We also designate structure that develops on KI/I treatment of nylon-6 as γ-phase. The γ-phase exhibits a sharp peak with a shoulder at the higher angle side, and *d*-spacings are at about 0.40 and 0.415 nm. The structures that exhibit *d*-spacing similar to the γ-phase but transform into the α-phase on annealing are designated as pseudohexagonal phase to distinguish them from the γ-phase, which in general obtained by KI treatment or by high-speed spinning.

The existing studies[17,18] that deal with crystalline transition in nylon-6 have been made on heating precrystallized samples having the α-phase and looked at the transition on heating from room temperature. In the present paper we report the results of the study on the crystallization of nylon-6 from the melt state and the crystalline transition 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. Furthermore, the α-phase has been transformed into the γ-phase by KI/I aqueous solution treatment, and the behavior of the γ-phase with temperature has also been studied for the first time.

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Experimental Section

Nylon-6 pellets (Akulon K2 2D grade, IV = 0.76 dL/g) were obtained from Century Enka, India. The X-ray diffraction experiments were performed using a Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator with a copper target and a wide-angle powder goniometer fitted with a high-temperature attachment. The generator was operated at 40 kV and 150 mA. All the experiments were performed in the reflection mode. 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 within 20 °C of the required set temperature, the cooling/heating rate was automatically reduced to 2 °C/min to minimize the over shooting of the set temperature. The temperature was maintained within 1 °C of the set temperature thereafter. The diffraction pattern was collected while the sample temperature was held constant, and the data were acquired in 5 min. To avoid degradation, the sample was kept under vacuum during experiment.

In situ crystallization studies had been made only at temperatures close to melting temperature because at these temperatures the crystallization rate of the nylon-6 was low, and the sample was still in an amorphous state after cooling from the melt. The crystallization temperature (T_C) was 210 °C. The development of the crystalline structure during 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 then heated to melting. The change in structure was monitored during cooling and heating by scanning at regular temperature intervals. The positions of the peaks were fixed by deconvoluting the peaks using Rigaku multipeak separation software available with the diffractometer system. The amorphous peak profile was assumed to be the same as the diffraction pattern of the melt at 240 °C.

The low cooling rate of the hot stage made in situ crystallization below 200 °C not possible because the sample crystallized before reaching the indented crystallization temperature. Hence, a different method was followed for the crystallization at lower temperatures. The copper block with thin film of the sample was heated above the melting temperature and quickly transferred to the Mettler hot stage (FP 82), which was maintained at the crystallization temperature. The crystallization temperatures were 140 and 180 °C. After the crystallization in the Mettler hot stage, the sample was transferred to the X-ray hot stage, and the change in structure was monitored during heating by scanning at regular temperature intervals.

Thin nylon-6 films were treated with KI/I aqueous solution to convert the α-phase into the γ-phase according to the procedure reported elsewhere.[4] The treated samples were loaded in the hot stage and heated to the melt. During heating the structure was monitored by scanning at regular temperature intervals. In some experiments the samples were annealed at high temperatures, and the structure was monitored on cooling to RT.

Results

The isothermal crystallization behavior of nylon-6 at 210 °C as followed by WAXS is shown Figure 1a. The first scan after reaching the crystallization temperature 210 °C shows traces of crystalline peaks, which develop rapidly with time. It is clearly seen from Figure 1a that the diffractograms show two peaks at $2\theta = 21.30°$ and 22.38°, and the *d*-spacing are 0.417 and 0.397 nm, respectively. The two-peak nature of the diffractogram indicates that the sample has crystallized in the α′-phase. The room-temperature structure of α-phase is monoclinic,[1] and the high-temperature phase is also considered to be monoclinic.

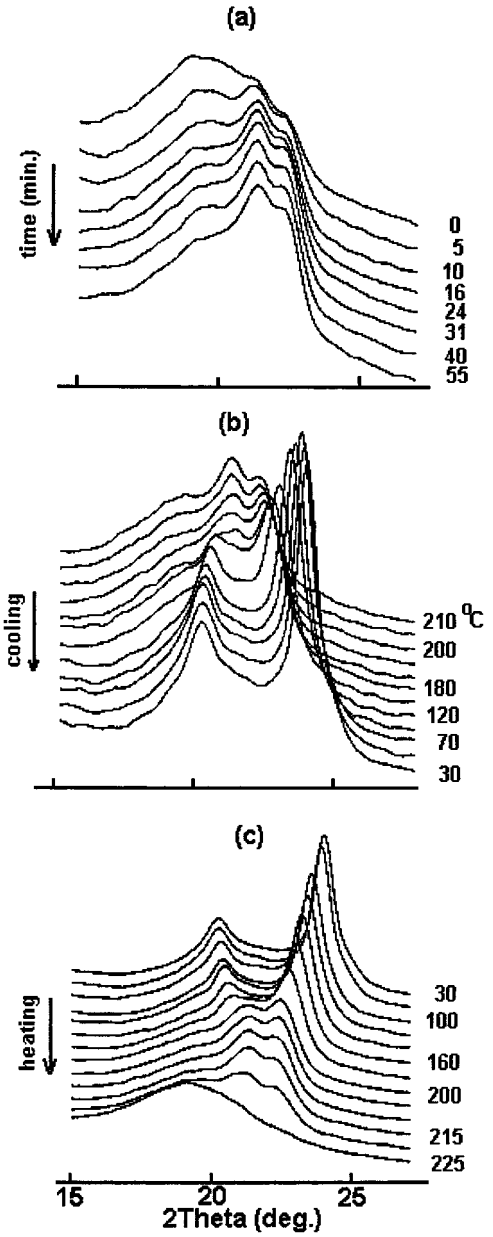

Figure 1. X-ray diffraction pattern obtained during (a) the isothermal crystallization of nylon-6 at 210 °C, (b) cooling from 210 °C, and (c) heating from room temperature to melting.

The behavior of diffractograms and the *d*-spacings on cooling from T_c to room temperature is shown in Figure 1b and Figure 2a, respectively. It is seen from Figure 1b that on cooling from the crystallization temperature the two-peak nature of the diffractogram is preserved, and *d*-spacings of the high-temperature phase show small decreases with decrease in temperature. However, a new peak at $2\theta = 20.79°$ appears at about 190 °C and becomes very prominent with decreases in temperature. At the same time the peak at $2\theta = 21.30°$ of the high-temperature structure disappears at about 150 °C when the new peak at $2\theta = 20.79°$ starts dominating. The *d*-spacing, 0.427 nm, of the new peak at $2\theta = 20.79°$ shows an increase with decreasing temperature while the *d*-spacing 0.397 nm (corresponding to $2\theta = 21.30°$) shows a decrease with decreasing temperature. At room temperature the peaks are at $2\theta = 20.17°$ and 23.98°, and the corresponding *d*-spacing are 0.440 and 0.371

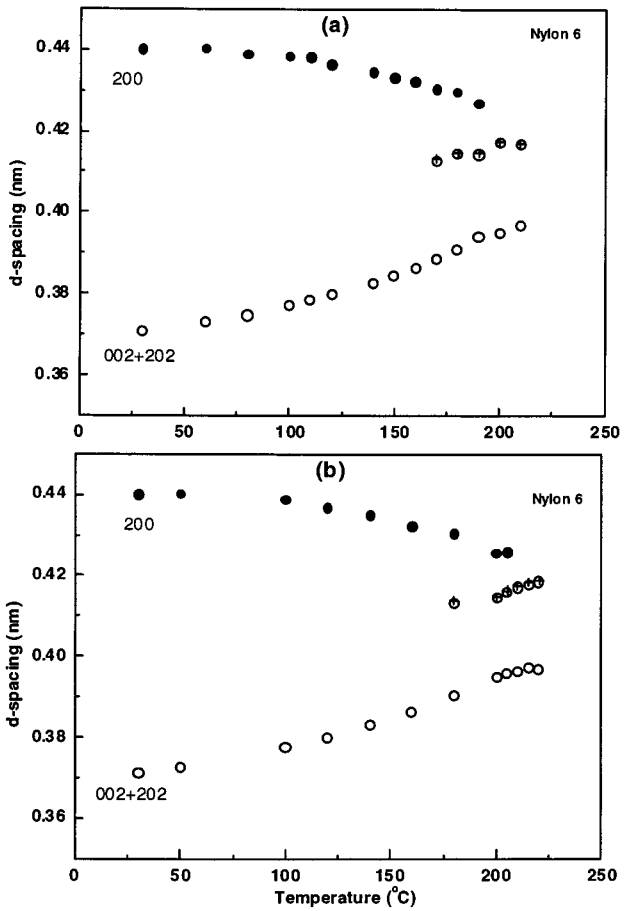

Figure 2. Change in *d*-spacing for nylon-6 with temperature during (a) cooling from 210 °C to RT and (b) heating from RT to melting.

nm, respectively. The peaks are indexed as the 200 and 002/202 reflections of the room-temperature monoclinic structure. It is evident from the behavior of the diffraction pattern and *d*-spacings that the high-temperature α′-phase transforms into low-temperature monoclinic structure on cooling. The transformation starts at about 190 °C and completes at about 150 °C. In this temperature range both the structure coexist.

On heating this sample from room temperature to melting the 200 and 002/202 peaks moves closure to each other with increasing temperature as shown in Figure 1c and the *d*-spacing in Figure 2b. A new peak appears at about 150 °C between the two peaks, and the 200 reflection of the room-temperature monoclinic structure vanishes at about 190 °C, indicating the transformation of room-temperature monoclinic structure to the high-temperature α′-phase. The sample melts in the high-temperature α′-phase. The volume fraction of the diffracted intensities of the reflections, during heating from the room temperature, is shown in Figure 3.

The behavior of diffraction patterns and *d*-spacing depend on the crystallization conditions. Figure 4 shows the diffraction patterns and *d*-spacings on heating of the samples which have been crystallized at 140 and 180 °C from the melt. It is evident from the diffraction pattern that the crystallized samples (the *d*-spacing 0.438 and 0.376 nm) have the α-phase at room temperature. Upon heating, the reflections 200 and 002/202 move close to each other and appear to become a single peak at about 150 °C for the sample crystallized at 140

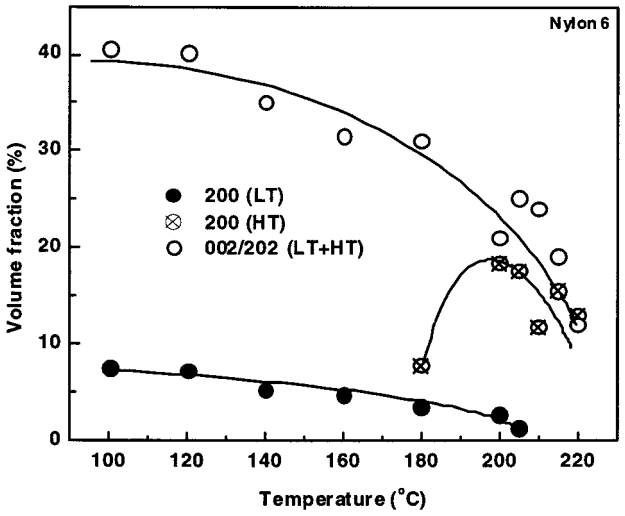

Figure 3. Variation of the volume fractions of the reflections on heating to melt.

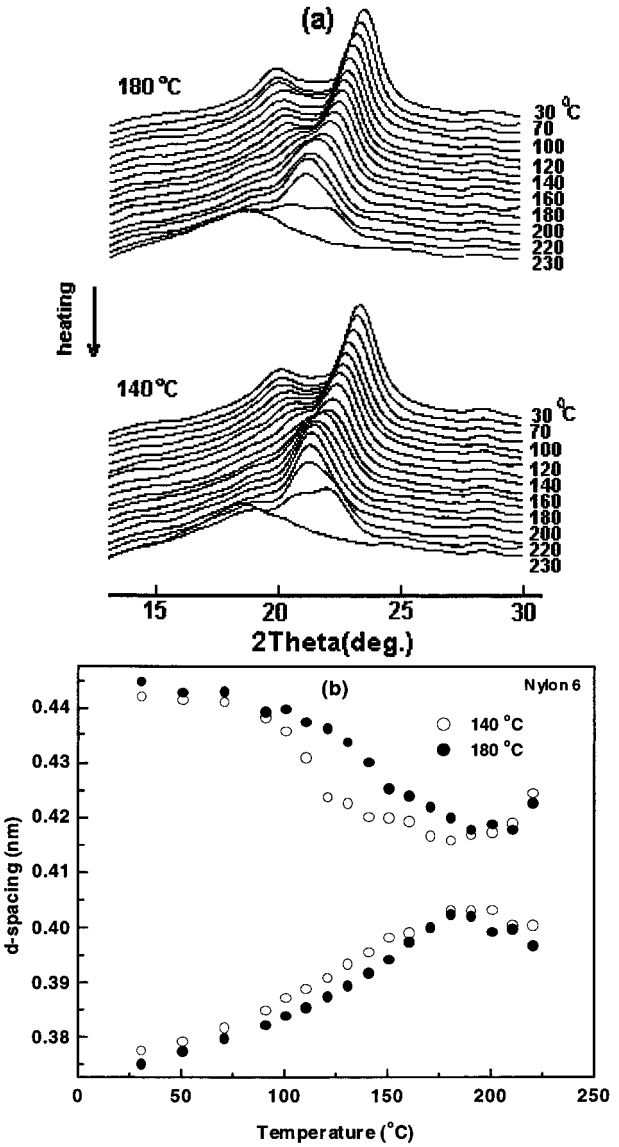

Figure 4. Behavior of (a) X-ray patterns and (b) *d*-spacing on heating nylon-6, which has been crystallized at 140 and 180 °C.

°C and at about 170 °C for the sample crystallized at 180 °C. However, deconvolution of the pattern shows

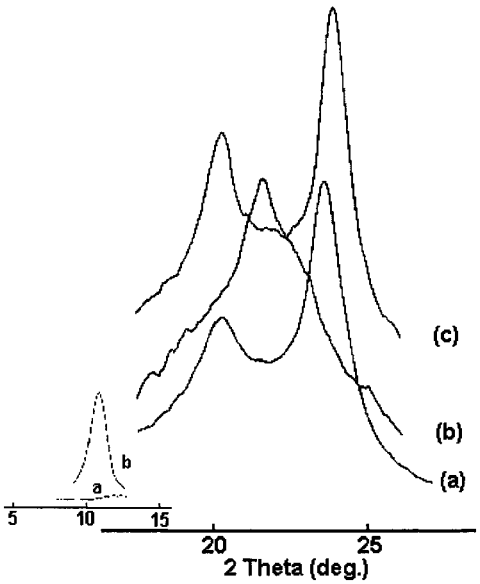

Figure 5. Diffractograms of the nylon-6 sample (a) before KI/I treatment, (b) after KI/I treatment, and (c) after melting the KI/I treated sample and recrystallization of at 210 °C. All patterns are at room temperature. The inset shows the behavior of the 020 peak.

that the peaks never coalesce into a single peak but remains separate, and the *d*-spacing are 0.418 and 0.400 nm. The fwhm (full width at half-maximum) of the peaks does not show appreciable variation. This indicates a crystalline transition at about 150 °C from RT α-phase to pseudohexagonal phase for the sample crystallized at 140 °C. However, the peaks again separate into two when the temperature is increased above 190 °C, indicating that the structure once again transformed into an α′-phase. The shape of the diffraction patterns and *d*-spacing above 190 °C temperature appears similar to the α′-phase discussed in the earlier paragraph. The sample crystallized at 180 °C; the pseudohexagonal phase exists over a small temperature range from about 180 to 190 °C. Above 190 °C, the pseudohexagonal phase transforms into the α′-phase as in the case with the sample crystallized at 140 °C.

The diffractograms of the sample before and after KI /I treated are illustrated in Figure 5. The diffractogram of the KI/I treated sample melted and recrystallized at 210 °C is also shown. The sample before the KI/I treatment shows peaks at $2\theta = 20.25°$ and 23.50° showing the presence of α-phase. On treating with KI/I solutions these peaks vanish, and a new peak appears at $2\theta = 21.47°$ (001 reflection) with a shoulder. Deconvolution of the peaks shows that the shoulder is due to a peak at 22.61° (200/$\bar{2}$01 reflection). Also, the peak 020 at $2\theta = 11°$ becomes prominent, while in the α-phase it is not visible. These changes indicate that the structure has transformed into the γ-phase. However, on recrystallizing at 210 °C after melting, the peaks reappear at $2\theta = 20.20°$ and 23.80° and the peak at $2\theta = 11°$ disappears, indicating that the sample once again crystallized in the α-phase.

The variation of the diffractogram and the *d*-spacing of the γ-phase on heating from room temperature to melting are shown in Figure 6 At room temperature, the characteristic reflections 001 and 200/$\bar{2}$01 of the γ-phase occur at 21.47° and 22.61°. The corresponding *d*-spacing are 0.414 and 0.393 nm. On heating to higher temperatures, the reflection 200/$\bar{2}$01 moves closer to the

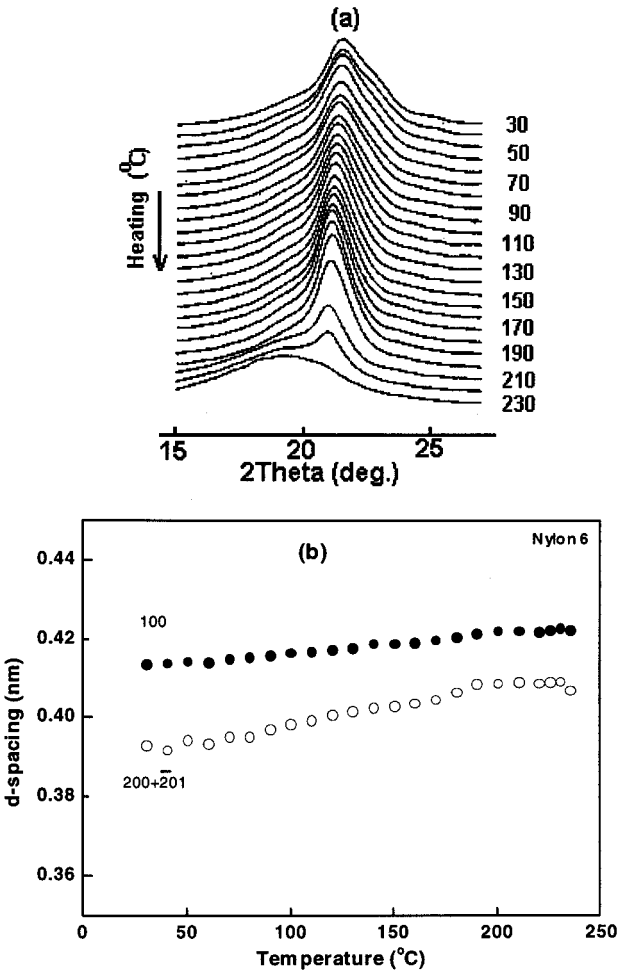

Figure 6. Behavior of the (a) X-ray diffraction patterns and (b) *d*-spacing of the γ-phase of nylon-6 on heating to melt.

main peak, while the position of the reflection 001 does not change significantly. These peaks disappear on melting without coalesce into a single peak, indicating that the sample melted in the γ-phase. These changes are reflected in *d*-spacings of these reflections and illustrated in Figure 6b where the variation of *d*-spacing on heating is plotted. The 001 reflection also does not exhibit any change with increasing temperature except for small increase in *d*-spacing due to thermal expansion and disappears on melting. The fwhm's of the reflections are shown in Figure 7, and the fwhm decreases with increase in temperature, indicating sharpening of the reflections on heating.

The behavior of the patterns is slightly different if the sample is annealed at temperatures below the melting point and then cooled to RT. Figure 8 shows diffraction pattern and *d*-spacing of the sample annealed at 200 °C and then cooled to RT. The diffraction pattern and *d*-spacing of the reflections 001 and 200/$\bar{2}$01 remain invariant on cooling except a small decrease in *d*-spacing due to thermal contraction. The diffraction pattern and *d*-spacing do not change on subsequent heating, except for small increase in *d*-spacings due to thermal expansion.

Discussion

The key observation in this work is the difference in the behavior of α-phase and γ-phase of KI/I-treated nylon-6 samples with temperature. In situ high-tem-

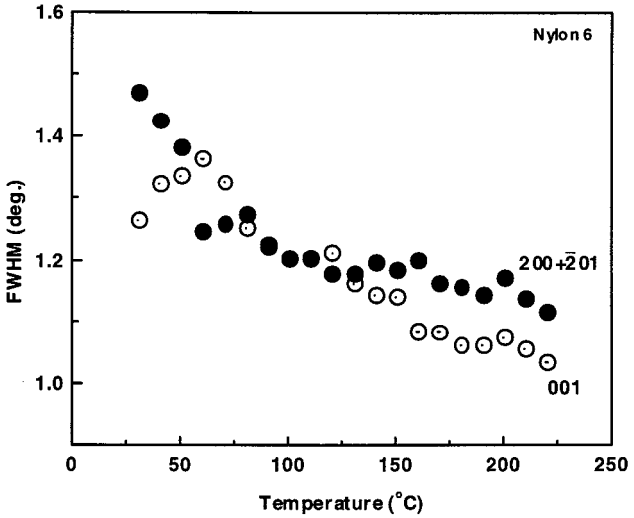

Figure 7. Behavior of fwhm of the reflections of the γ-phase of nylon-6 on heating to melt.

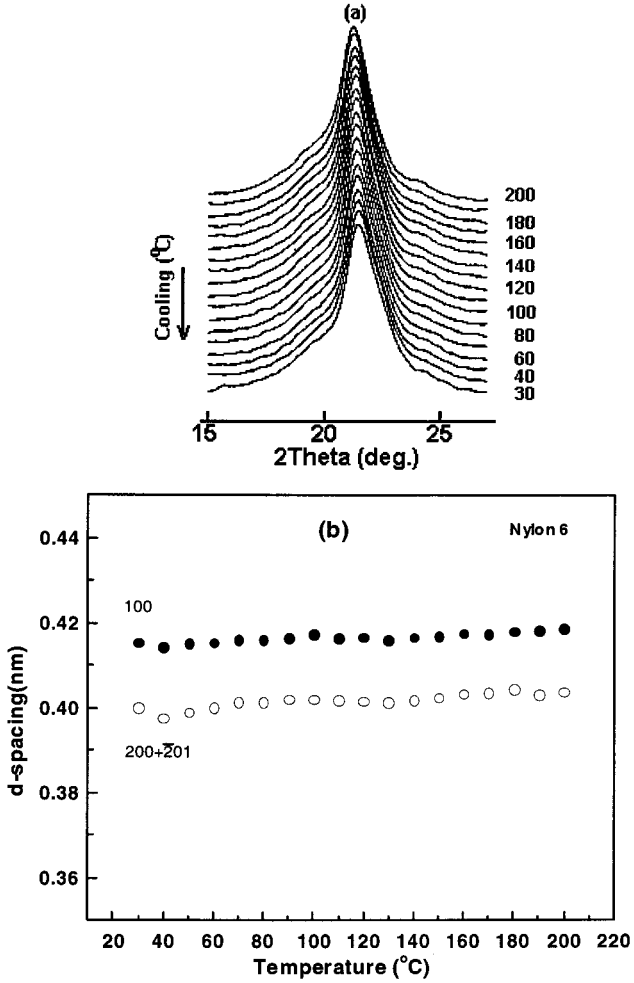

Figure 8. Behavior of the (a) X-ray diffraction patterns and (b) *d*-spacing of the γ-phase of nylon-6 on cooling after annealing at 200 °C.

perature X-ray diffraction studies on the crystallization of nylon-6 from the melt shows that it crystallizes in the HT α′-phase and transforms into RT α-phase on subsequent cooling. This behavior is in agreement with the general behavior of nylon crystallization from the melt and on subsequent cooling. The nylon-6,6 and nylon-4,6 crystallize into to the γ-phase when crystallized from the melt and transforms into the α-phase on subsequent cooling.[15] On the other hand, nylon-6,10 and -6,12 also crystallize into high-temperature α′-phase and then transform into RT α-phase on cooling.[15] Nevertheless, nylon-6 shows difference during the transition, which has not been observed with other nylons. In the case of nylon-6 the transition takes place with the appearance of a new peak and disappearance of a existing peak on cooling. The transition occurs over a temperature range from 190 to 170 °C during cooling and 180 to 205 °C on heating. In this temperature range both the high-temperature phase and low-temperature phase coexist. Murthy et al.[17] report a transition range from 80 to 170 °C; however, it may be noted that the crystallization history of their sample was different. The behavior of α-phase and α′-phase with temperature is different. The main change is the separation of hydrogen-bonded chains in the sheet. The α′-phase has a shorter distance between the hydrogen-bonded chains than in the α-phase and decreases with decreasing temperature, while in the case of the α-phase it increases with decrease in temperature. Another noticeable feature is the variation of intensity of the 200 and 002/202 peaks. In the α-phase the intensities of these peaks decrease with increases in temperature. In the phase transition temperature range the 002/202 peak, which has not been resolved into low- and high-temperature components, shows a smoother variation in intensity. On the other hand, the 200 peak, which has been resolved into low- and high-temperature components, behaves differently. The intensity of the 200 peak of the α-phase, which is almost 4 times lower than the intensity of 002/202 peak, decreases with increasing temperature and disappears after the structure transforms into α′-phase. On the other hand, the 200 peak of the α′-phase increases very rapidly after the transition, and both reflections have similar intensities. A similar observation has also been reported by Murthy et al.[17]

The samples crystallized at 140 and 180 °C show marked difference in the behavior of the X-ray diffractograms and *d*-spacing on heating when compared to the sample crystallized at 210 °C. On heating the RT α-phase first transformed into a pseudohexagonal phase at temperatures close to crystallization temperature and remains in that phase until 190 °C and then transforms into the HT α′-phase. The temperature range in which the pseudohexagonal phase is stable appears to be dependent on crystallization conditions. In the sample that has been crystallized at 140 °C, the pseudohexagonal phase occurred at about 150 °C and transformed into the HT α′-phase at 190 °C. On the other hand, the sample crystallized at 180 °C; the pseudohexagonal phase existed over a small temperature range from 170 to 190 °C. The pseudohexagonal phase may be identified with the phase that had been obtained on rapid cooling from the melt and can be converted into α-phase on annealing.[8−10] It is apparent that nylon-6 crystallizes in the HT α′-phase above 190 °C, and on cooling it transforms into the RT α-phase. On heating, it transforms directly into the HT α′-phase at about 190 °C. On the other hand, if it is crystallized below 190 °C and on heating the α-phase passes through the pseudohexagonal phase before transforming into the HT α′-phase before melting. Nylons-6,10 and -6,12 also showed a similar crystalline transition behavior.[15]

The γ-phase obtained by KI/I treatment of the α-phase of nylon-6, on the contrary, does not show any crystal-

line transition on heating or on cooling after annealing at 200 °C. In fact, the γ-phase as obtained from KI/I treatment becomes more perfect on heating, and after perfection the structure does not respond to temperature except for thermal expansion (Figure 8). However, on melting the hydrogen bonds break and the γ-phase disappears. It has also been observed that further crystallization of the melt at 210 °C yields only the α′-phase, which on cooling transforms into the α-phase. The diffraction patterns are similar to the patterns of the α-phase shown in Figure 1a,b. Miyasaka and Makishima[4] have observed that the γ-phase transforms into the α-phase under the application of stress in nylon-6 fiber. Murthy[5] also observed a similar transition in fibers having the γ-phase and terms the α-phase as a metastable phase, which is different from the RT α-phase. However, the γ-phase may be converted[5,6,17] into the α-phase by annealing in steam at 160° C or on melting and recrystallization. These indicate that the γ-phase is a stable phase and can exist independent of the α-phase, though it is formed only under severe conditions like high-speed spinning or KI/I solution treatment. The coexistence of the α- and γ-phase on high-speed spun fibers may be attributed to the stability of both the phases.

The stability of the γ-phase may be due to its structure. The α-phase of nylon-6 has antiparallel chains in the sheet and hydrogen bonds link them. The chain folds are in the plane of the sheet and link the chains within the sheet. In the case of γ-phase, the only change is that the chains are twisted and the hydrogen bonds are formed between the parallel chains and the sheets are connected by chain folding.[7] In this structure, the sheets cannot move away from each other on heating, as in the case of α-phase, leading to little change in *d*-spacing on heating or cooling.

Conclusions

The in situ X-ray diffraction studies on the crystallization of nylons-6 provide new information on crystalline transitions on cooling and heating. Nylons-6 crystallize directly into HT α′-phase if crystallized from the melt in a narrow temperature range between 200 °C and melting temperature. This structure transforms into the RT α-phase on cooling, and the transition occurs over a temperature range. On heating, the RT α-phase transforms into the α′-phase at about 190 °C and melts in that phase. If the sample is crystallized at temperatures below 190 °C from the melt, then on subsequent heating the α-phase first transforms into a psuedohexagonal phase and then into the α′-phase at about 190 °C before melting. The temperature range in which the pseudohexagonal phase can exist depends on crystallization conditions, and the higher temperature limit is about 190 °C.

The α-phase of nylon-6 can be transformed into the γ-phase by treating nylon-6 in KI/I aqueous solution. The γ-phase does not show any crystalline transition on heating and melts in the γ-phase. The behavior of the γ-phase with temperature appears to be different from the general behavior of nylon structures when subjected to a temperature program.

The γ-phase may be distinguished from the pseudohexagonal structure, even though both have similar *d*-spacings. The pseudohexagonal structure can be transformed into the α′-phase by annealing it above 200 °C but below the melting temperature and on subsequent cooling to room-temperature results in the α-phase. But the γ-phase can be transformed into the α-phase only by melting and recrystallization.

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