# Communications to the Editor

## Crystalline Transitions in Nylon 12

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**Introduction**. Nylons exhibit crystalline transition on cooling or heating. The crystalline transition in nylon 6 6 has been most extensively studied among all nylons. Upon heating nylon 6 6, the structure shows a crystal-to-crystal transition and is known as a Brill transition.[1−7] In nylon 6 6 the room temperature triclinic structure transforms into a pseudohexagonal structure at elevated temperatures. The Brill transition in nylon 6 6 is clearly displayed in X-ray diffraction studies, as two prime strong reflections at *d* spacings 0.37 and 0.44 nm merge into a single reflection at the transition. The Brill transition has also been reported for many even−even nylons.[8−12] Recent studies[9] on nylons 4 6, 6 10, and 6 12 have shown that these nylons exhibit the Brill transitions and other crystalline transitions depending on crystallization conditions. There are few reports on the temperature-induced crystalline transition in even nylons. Murthy[7] and co-workers have observed that the room temperature (RT) monoclinic structure of nylon 6 transforms into a high-temperature (HT) monoclinic structure on heating from RT.[3] Vasanthan et al.[10] have reported changes in infrared spectra of nylon 6 and 6 6 during transition.

The nylons 6 6,[13] 6 10, and 6 12[14] have triclinic structure at room temperature while nylons 6[15] and 4 6[16] have similar but different monoclinic structures. All these structures are called α-phases and show characteristic two peaks in the diffractograms at RT, and the *d* spacings are at about 0.37 and 0.44 nm. These spacings are due to the intersheet distance between the sheets and the projected interchain distance with in the sheet, respectively. The nylons can also exist in hexagonal structure and is known as $\gamma$-phase. The characteristic of $\gamma$-phase is that it exhibits only one strong reflection corresponding to *d* spacing at about 0.42 nm. We designate all the structures that exhibit two distinct peaks having *d* spacing at about 0.37 and 0.44 nm as α-phase and only one peak at *d* spacing at about 0.42 nm as $\gamma$-phase or hexagonal phase. The structures that show two close spacings having values other than 0.37 and 0.44 nm are designated as α′-phase, which is different from the room-temperature α-phase.

The α-phase of nylon 12 is monoclinic,[17,18] and the room-temperature phase of nylon 12 appears to depend on the crystallization conditions. The samples crystallized by slow cooling and rapid quenching from the melt show $\gamma$-phase at room temperature.[21] The single-crystal mats[22] and drawn and rolled samples[22] show α′-phase at room temperature as the spacings are very close. However, nylon 12 crystallized at high temperature and pressure exhibits both α- and $\gamma$-phase at room temperature.[20,21] In this communication we report for the first time the crystallization of nylon 12 into α′-phase when crystallized from the melt and its subsequent transition into $\gamma$-phase while cooling to room temperature.

**Experimental Section.** Nylon 12 was obtained from Aldrich and used as received. The X-ray diffraction experiments were performed using a Rigaku Dmax 2500 diffractometer system consisting of a rotating anode generator and wide angle powder goniometer fitted with a high-temperature attachment. The sample holder was a copper block, and a thin film of nylon 12 was formed on that block by melt pressing the sample. The sample is initially heated in the hot stage well above the melting temperature of the sample and cooled to the crystallization temperature. The sample was cooled/heated at 20 °C/min, and when the sample temperature reached within 20 °C of the set temperature, the cooling/heating rate was reduced to 2 °C/min to minimize the over shooting. The crystallization was performed at 170 and 160 °C. For temperatures below 160 °C, the sample crystallizes before reaching the intended crystallization temperatures because of the low cooling rates of the hot stage. 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 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. The positions of the peaks were fixed by deconvoluting the peaks using Rigaku multipeak separation software available with the diffractometer system.

**Results and Discussion.** The diffraction patterns obtained during isothermal crystallization of nylon 12 at 170 °C are shown in Figure 1a. The amorphous sample slowly crystallizes with increase in crystallization time. The diffraction pattern shows two distinct crystalline peaks: a small peak at $2\theta = 20.353°$ and a sharp bigger peak at $2\theta = 21.018°$. The corresponding *d* spacings of these reflections are 0.436 and 0.423 nm, respectively. The two-peak nature of the diffractograms shows that the sample crystallized into α′-phase, as the spacings are very close. The behavior of diffractograms on cooling from crystallization temperature to room temperature is shown in Figure 1b. It is seen from the figure that the small peak at $2\theta = 20.353°$ shows decrease in intensity and shifts closer to the bigger peak. The smaller peak vanishes at about 140 °C, and the diffractograms show only the strong peak on further cooling to room temperature (RT). The behavior of *d* spacing of the peaks during cooling to RT is shown in Figure 2a. The *d* spacings show a decreases with

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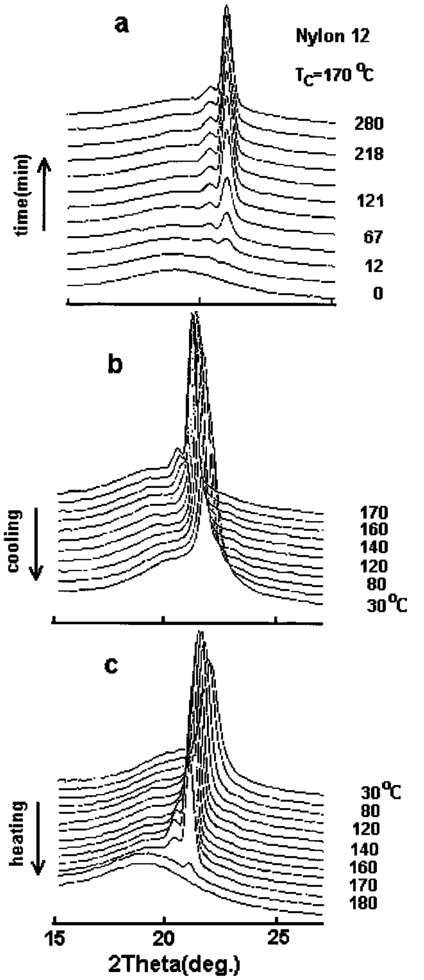

**Figure 1.** X-ray diffraction pattern obtained during (a) the isothermal crystallization of nylon 12 at 170 °C, (b) cooling from 170 °C, and (c) heating from room temperature to melting.

decreasing temperature. The *d* spacing due to the small peak at 0.436 nm disappears at about 140 °C. The *d* spacing, 0.423 nm, due to the strong peak shows a small decrease and reaches a value of 0.42 nm. The disappearance of the small peak indicates a phase transition, and in this case it is from α′-phase to γ-phase on cooling from crystallization temperature to room temperature. The behavior of diffractograms and *d* spacings on heating the sample from RT to melting is shown in Figures 1c and 2b, respectively. It is apparent from these figures that the phase transition and variation in *d* spacings are reversible on heating, and the α-phase is preserved until melting. The sample crystallized at 160 and 175 °C also shows behavior similar to the sample crystallized at 170 °C.

The key observation of this work is the crystallization of nylon 12 in α′-phase and its subsequent transformation into γ-phase on cooling to room temperature. This is the first instance such a transformation is observed in nylon 12. The α′-phase of nylon 12 is monoclinic, and the high-temperature (HT) α′-phase is also assumed to be monoclinic. The present finding of HT α′-phase transformation into γ-phase on cooling confirms the earlier reports that nylon 12 has hexagonal structure at room temperature[16,17,19] when crystallized from the melt. Hiramatsu et al.[21] observed that α-phase obtained by high-pressure crystallization transforms into γ-phase on annealing at 150 °C. However, the structural characterization had been done at room temperature. The even nylons such as nylons 6 and 12 have antiparallel chains in the α-phase and parallel chains in γ-phase. Aharoni[17] sketches a scheme for the transformation of α-phase into γ-phase without local melting and recrystallization for these nylons.

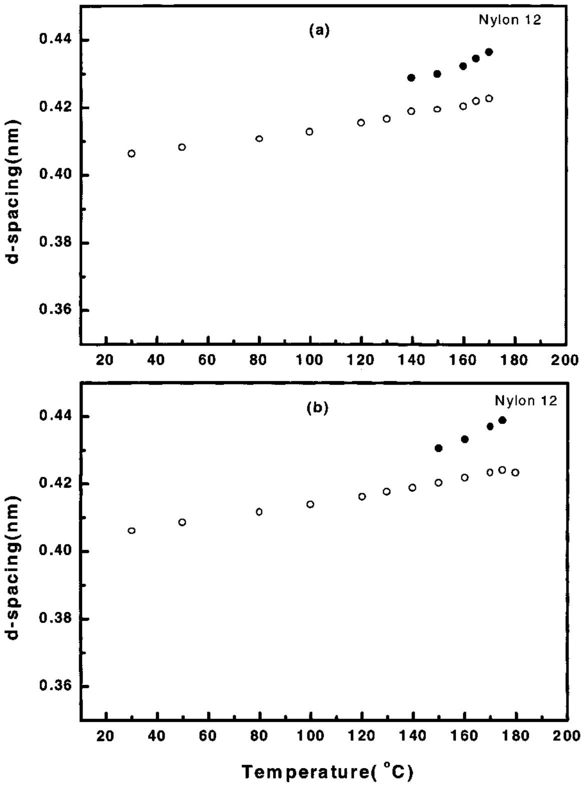

**Figure 2.** Change in *d* spacing for nylon 12 with temperature (a) cooling from 170 °C to RT and (b) heating from RT to melting.

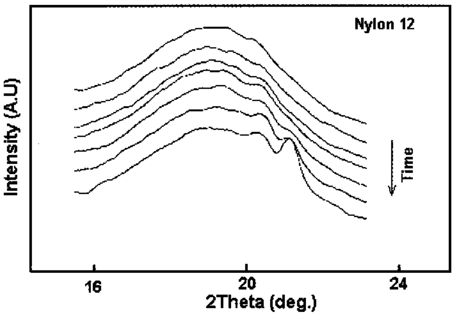

**Figure 3.** Diffraction pattern obtained during the initial stages of crystallization of nylon 12 at 175 °C.

At crystallization temperature (170 °C), the spacing 0.436 nm relates to the small peak and 0.426 nm corresponds to the larger peak. It can be seen from Figures 1 and 2 that the bigger peak shows little variation during the α′- to γ-phase transition. It follows that the spacing 0.426 nm corresponds to γ-phase and is the projected interchain distance within the sheet. Then in the α′- phase, the 0.436 nm corresponds to the intersheet distance. In the case of even−even nylons the intersheet distance is always equal to (in the case γ-phase, 0.42 nm) or less than the projected interchain distance within the sheet (α-phase). Dosière[22] also finds crossing of these two spacings on heating doubly oriented nylon 12 samples. The crystallization of nylon 12 into HT α′-phase is not an isolated case, and it has been shown[9] that nylons 6 10 and 6 12 also crystallize into HT α′-phase when crystallized from the melt. But unlike nylon 12, these nylons transform into RT α-phase on cooling. It is not known at this stage that the RT α-phase present in the high-pressure crystallized material[20,21] is related to the HT α′-phase reported here.

The diffractograms during the initial stages of crystallization of nylon 12 at 175 °C are given in Figure 3 and show an interesting feature. The smaller peak at $2\theta = 20.353°$ (0.436 nm spacing) appears first during the start of the crystallization, and the stronger peak at $2\theta = 21.018°$ (0.423 nm spacing) appears later which grows with time. This could indicate that the nylon 12 crystallizes into a high-temperature hexagonal structure (called $\gamma'$-phase to distinguish from the RT $\gamma$-phase) initially but transforms into α′-phase with progress in crystallization. The samples crystallized at 160 and 170 °C also indicate a similar feature; however, it is more readily apparent for the sample crystallized at 175 °C due to lower crystallization rate. The *d* spacing is 0.436 nm and is unusually large when compared with the 0.42 nm of the $\gamma$-phase. Though the exact reasons for this high *d* spacing value are unknown at this stage, it may be speculated to the absence of hydrogen bonds at early stages of crystallization. Time-resolved wide-angle X-ray scattering and small-angle X-ray scattering studies using synchrotron radiation source can give more information on the nature of crystallization and subsequent transformation during the course of crystallization and then on cooling to room temperature.

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