

Phase Stability and Melting Behavior of the α and γ Phases of Nylon 6

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ABSTRACT: The phase stability and melting behavior of nylon 6 were studied by high-temperature wide-angle X-ray diffraction and differential scanning calorimetry (DSC). The results show that most of the α phase obtained by a solution-precipitation process [nylon 6 powder (Sol-Ny6)] was thermodynamically stable and mainly melted at 221°C; the double melting peaks were related to the melt of α crystals with different degrees of perfection. The γ phase formed by liquid nitrogen quenching (sample LN-Ny6) melted within the range 193–225°C. The amorphous phase converted into the γ phase below 180°C but into the high-temperature α phase at 180–200°C. Both

were stable over 220°C. α - and γ^* -crystalline structures were formed by annealing but were not so stable upon heating. Typical double melting peaks were shown on the DSC curve; melt recrystallization happened within the range 100–200°C. The peak at 210°C was mainly due to the melting of the less perfect crystalline structure of the γ phase and a fraction of the α phase; the one at 219°C was due to the high-temperature α - and γ -phase crystals. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1885–1891, 2011

Key words: crystal structures; phase behavior; polyamides

INTRODUCTION

Nylon 6 is a typical semicrystalline polymer with excellent physical and mechanical properties. It is believed that its crystal structures and morphologies are extremely important to the properties of nylon 6; these depend on the processing and crystallization conditions.¹ Nylon 6 exhibits basically two crystalline structures, namely, the α and γ phases. The α phase has a monoclinic structure with fully extended nylon 6 chains, and hydrogen bonds are formed

between antiparallel chains with the ethylene segments and amide groups in the same plane; this results in a sheetlike form. The γ phase is composed of pleated chains, where the hydrogen bonds are formed between parallel chains, and the direction of the intermolecular hydrogen bonds is perpendicular to the plane of the carbon framework.^{2,3} A generally accepted view is that the α phase is more thermodynamically stable and can form by solution casting, annealing, crystallization at high temperatures, or slow cooling from the molten state; however, at rather low crystallization temperatures, rather high cooling rates, or a high spinning speed, nylon 6 tends to crystallize in the γ phase, which is regarded as less thermodynamically stable. Transitions happen between the α phase and γ phase when various treatment methods are used. For instance, the γ phase can convert into the α phase by melting followed by recrystallization,⁴ by annealing at 160°C in a saturated-steam atmosphere,⁵ or by the application of stress at room temperature.⁶ The α phase can convert into the γ phase if it is treated with a KI/I aqueous solution.⁷

The melting behavior and crystalline structures of nylon 6 and its composites, especially systems of nylon 6 nanocomposites, have been studied extensively by differential scanning calorimetry (DSC) and room-temperature wide-angle X-ray diffraction

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TABLE I
Sample Details

Sample	Description
Sol-Ny6	Nylon 6 powder precipitated from a formic acid solution
LN-Ny6	Melting samples quenched in liquid nitrogen
LNA-Ny6	Quenched samples annealed <i>in vacuo</i> at 190°C for 48 h

(WAXD) during the last several years.^{8–17} Multimelting peaks are usually observed on the DSC heating curves because of the complex crystalline structures, especially in the α - and γ -crystal phase coexisting systems. It is generally believed that the higher temperature melting peak is related to the melting of the α phase because of its thermodynamically stable character, and the lower temperature peak next to the higher one is due to the γ phase; sometimes, it just shows an unobvious shoulder peak.^{8–21} Furthermore, it was reported by McCrum et al.²² and Weigel et al.²³ that the multimelting peaks of nylon 6 can reach as many as five, with the assumption that the two of them correspond to the fusion of the α - and γ -phase crystals, and when the ascriptions are the same as discussed previously, the other melting peaks are supposed to correspond to the fusion of different perfect degrees of the α and γ phases.

However, as room-temperature WAXD can only show the diffraction pattern of crystal structures existing in materials, the phase stability of the α - and γ -crystal structures of nylon 6 have not been specifically studied so far, and the essence and ascription of the multimelting peaks were just explained on the basis of the understanding of the morphological structure of the α and γ phases mentioned previously.

In this article, high-temperature wide-angle X-ray diffraction (HTWAXD) and DSC were used to study the phase stability and melting behavior of nylon 6.

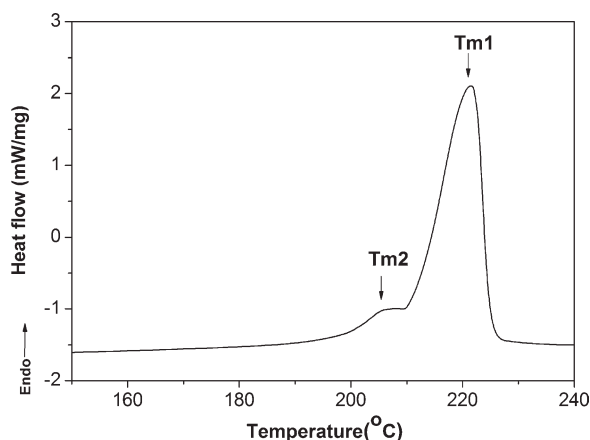


Figure 1 DSC melting traces of Sol-Ny6.

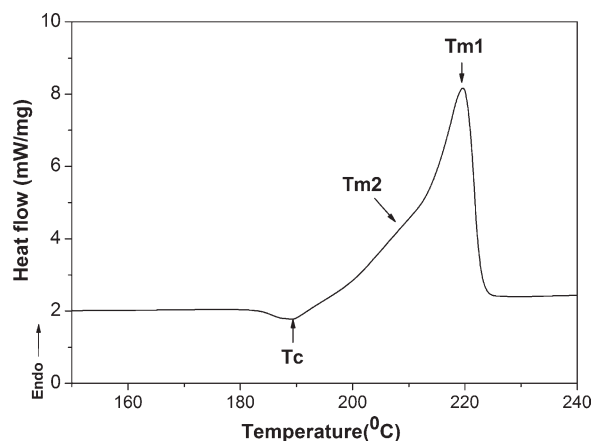


Figure 2 DSC melting traces of LN-Ny6.

Three samples with different crystal structures, α -phase, γ -phase, and the α - and γ -phase coexisting system, were prepared by different thermal processes. The experimental results gave a very clear picture of the phase stability of the α - and γ -crystal structures, and a more precise interpretation of the multimelting peaks was observed with the DSC curves, which were somewhat different from those in existing studies.^{9,12}

EXPERIMENTAL

Materials

Nylon 6 resin (UBE-1013E, low-viscosity grade, density (d) = 1.14 g/cm³) was provided by UBE, Ltd. (Japan). The original nylon 6 powder (Sol-Ny6) was obtained from a dissolved nylon 6 resin in formic acid that was precipitated in water. Sol-Ny6 was obtained after filtration and was dried *in vacuo*.

Specimen preparation

All samples were dried *in vacuo* at 80°C for 24 h to eliminate the absorbed water due to the high moisture absorption characteristic of nylons. Next, the powder was melted in a metal mold at 240°C for 5 min to prevent the affect of thermal history, and then, it was pressed into slices, quickly removed from the press and quenched into liquid nitrogen immediately to obtain quenched samples (LN-Ny6). The LN-Ny6 samples were annealed *in vacuo* at 190°C for 48 h and then cooled to room temperature. The annealed samples (LNA-Ny6) were thus obtained. The samples used in this study are summarized in Table I.

Instruments and measurements

DSC

DSC experiments were carried out on a TA Instruments Q10 calorimeter (New Castle, DE). Calibrations

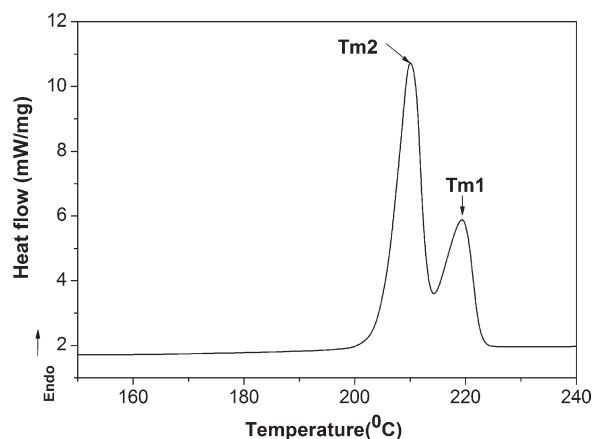


Figure 3 DSC melting traces of LNA-Ny6.

of temperature and heat enthalpy were performed with indium as the standard. The samples were heated from room temperature to 260°C at a constant heating rate of 10°C/min. All of the experiments were performed under a nitrogen atmosphere.

HTWAXD

HTWAXD experiments were performed on a Bruker D8 diffractometer (Madison, WI) fitted with a high-temperature attachment and a nitrogen cooling unit. Cu Kα radiation ($\lambda = 0.154 \text{ nm}$) was generated at an accelerating potential of 40 kV and a tube current of 40 mA. The samples were heated at a rate of 10°C/min, and when the temperature was within 5°C of the required temperature, the heating rate was reduced to 6°C/min to minimize overshooting of the set temperature. After the required temperature was reached, X-ray scanning was performed in the 2θ range from 5 to 35° at a scanning rate of 4°/min.

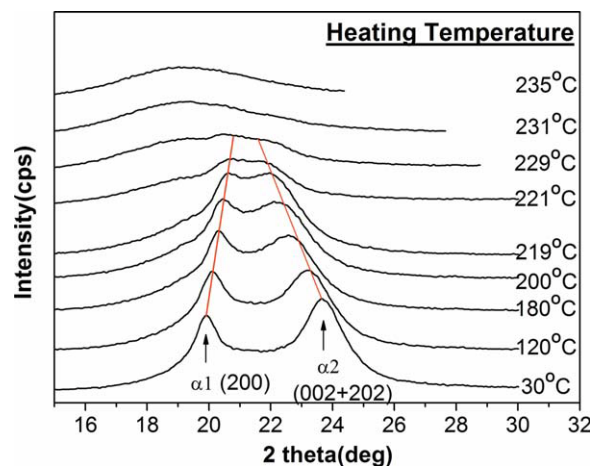


Figure 4 WAXD patterns of Sol-Ny6 at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

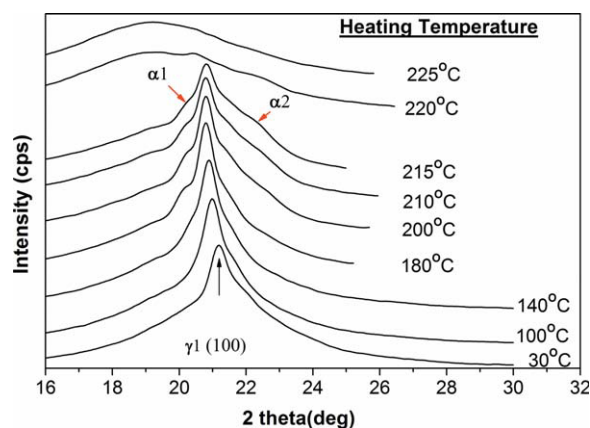


Figure 5 WAXD patterns of LN-Ny6 at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

General information about the crystal structures of the three samples

Figures 1, 2, and 3 show the DSC heating traces of Sol-Ny6, LN-Ny6, and LNA-Ny6, respectively, and Figures 4, 5, and 6 show the WAXD curves of the same three samples. According to the results of the DSC studies, we used the following equation to calculate the degree of crystallinity (X_c) for the three samples:

$$X_c = (\Delta H_{m \text{ nylon } 6} / \Delta H_{m \text{ nylon } 6 \text{ 100\%}}) \times 100\%$$

where $\Delta H_{m \text{ nylon } 6 \text{ 100\%}}$ is the melting enthalpy of perfect crystals of nylon 6 (185.8 J/g according to Inoue²⁴) and $\Delta H_{m \text{ nylon } 6}$ is the melting enthalpy of the samples. The results are shown in Table II.

As shown in Figures 4, 5, and 6, for the sol-Ny6 sample, WAXD showed that the crystal form was

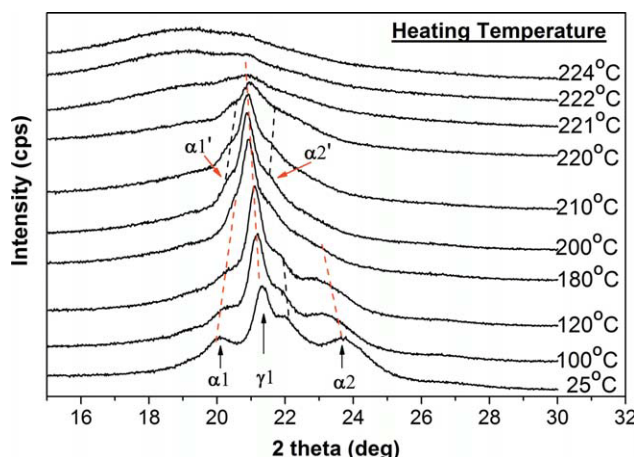


Figure 6 WAXD patterns of LNA-Ny6 at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Crystal Structure Data for the Samples

Sample	ΔH_m Nylon6 (J/g)	X_c (%)	R_α (%)	R_γ (%)
Sol-Ny6	56.2	30.2	100	0
LN-Ny6	41.2	22.2	0	100
LNA-Ny6	86.9	46.8	37.8	62.2

mainly the α -phase crystals; for LN-Ny6, it was mainly γ -phase crystals; and for LNA-Ny6, both α - and γ -phase crystals coexisted. The resulting plots of X-ray intensity versus 2θ were analyzed with the profile fitting program MDI Jade 5.0 (Livermore, CL) with a Gaussian peak shape, as shown in Figure 7. The crystalline proportions of the γ and α forms were calculated according to eqs. (1) and (2); the results are shown in Table II:

$$R_\gamma = \text{Area}(\gamma) / [\text{Area}(\gamma) + \text{Area}(\alpha)] \times 100\% \quad (1)$$

where R_γ refers to the crystalline proportions of the γ -phase crystals; $\text{Area}(\gamma)$ refers to the area of all the refraction peak of γ phase crystals; $\text{Area}(\alpha)$ refers to the area of all the refraction peak of α phase crystals.

$$R_\alpha = \text{Area}(\alpha) / [\text{Area}(\gamma) + \text{Area}(\alpha)] \times 100\% \quad (2)$$

where R_α refers to the crystalline proportions of the α -phase crystals.

$$\text{Area}(\gamma) = \text{Area}(\gamma_1) + \text{Area}(\gamma_2) + \text{Area}(\gamma_3)$$

where γ_1 , γ_2 , and γ_3 refer to the three refraction peaks of γ -phase crystals of Nylon 6; $\text{Area}(\gamma_1)$, $\text{Area}(\gamma_2)$, and $\text{Area}(\gamma_3)$ refer to the area of γ_1 , γ_2 , and γ_3 refraction peak respectively.

$$\text{Area}(\alpha) = \text{Area}(\alpha_1) + \text{Area}(\alpha_2)$$

where $\text{Area}(\alpha)$ refers to the area of all the α refraction peak; $\text{Area}(\alpha_1)$ refers to the area of α_1 refraction peak; $\text{Area}(\alpha_2)$ refers to the area of α_2 refraction peak.

Melting behavior and phase stability of nylon 6 prepared by the solution-precipitation process (Sol-Ny6)

The DSC heating curve of Sol-Ny6 precipitated from formic acid showed typical double melting peaks within 190–232°C, as shown in Figure 1. One was at the higher temperature, which was the main melting peak (T_{m1}), with a peak temperature of 221°C; the other was at the lower temperature, at about 206°C, and neighbored with T_{m1} as a shoulder melting peak (T_{m2}).

As mentioned in the Introduction, it seemed reasonable to conclude that this sample contained two crystal structures, one was the γ phase, which corresponded to the melting behavior at T_{m2} , and the other was the α phase, which corresponded to T_{m1} .^{8–17} However, from the HTWAXD patterns of this sample, as shown in Figure 4, one can see different results. At room temperature, there were two diffraction peaks at 19.9 and 23.6°, which were assigned to the (200) and (002)/(202) reflections of the α -phase crystals of nylon 6, respectively. It was clear that no γ phase was formed because the characteristic peak at 21° did not appear. So the two melting peaks on the DSC curve should correspond to the melting of a crystals with different degrees of perfection.

When this sample was heated from room temperature to 235°C, the (200) peak (α_1) and (002)/(202) peak (α_2) moved closer to each other but did not merge into a single reflection until the crystals melted, and there was no new diffraction peaks formed during heating. When the sample was heated to 180°C, the diffraction intensity of α_2 became weaker, whereas that of α_1 remained almost the same. When the temperature reached 219°C, the diffraction intensities of α_1 and α_2 were as strong as those at 180°C. Up to 221°C, the peak intensities became rapidly weaker and turned into two small but noticeable diffraction peaks. The two peaks disappeared completely and showed an amorphous diffraction when temperature reached 231°C.

According to the literature,^{8,9} the crystal d -spacing changes due to thermal expansion and contraction when the temperature is increased. In the α phase, the d -spacing of the (200) planes and (002)/(202) planes was due to the interchain distance within the sheet and the intersheet distance between the sheets, respectively. The interactions between the interchains and intersheets were formed mostly by hydrogen bonds. As a result, the change in d -spacing was due to the change of hydrogen-bond length.

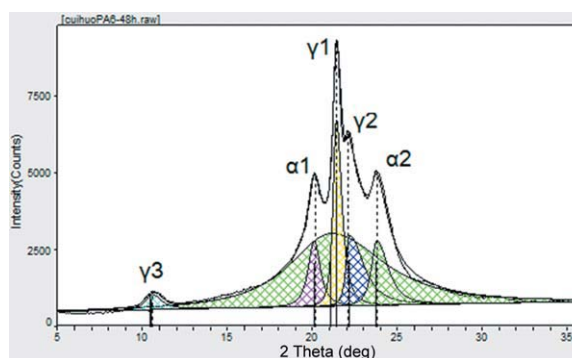


Figure 7 Profile analysis of the diffraction scans from the LNA-Ny6 sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Intensity of the γ_1 Reflection on Heating

Temperature (°C)	30	100	140	180
Intensity (cps)	8,422	10,160	10,472	10,873
Peak width at half-height	0.646	0.618	0.608	0.558

The (002)/(202) peak shifted to a lower diffraction angle, whereas heating increased the intersheet hydrogen-bond length because of thermal expansion. Although a shift to a higher angle of (200) peak meant a decrease in the interchain hydrogen-bond length, the two peaks did not merge into a single one; this indicated that the hydrogen bonds remained stable until melting, and the α phase with antiparallel chains did not convert into the γ phase with parallel chains. This confirmed that only thermal vibration of the molecules contributed to the changes in d -spacing.

The DSC curve (Fig. 1) showed no caloric effect from room temperature to 180°C; this signified that the sample did not melt below 180°C. However, the diffraction intensity of α_2 weakened obviously with heating to 180°C, as shown in Figure 4. The reasons for that were as follows:

1. The heat energy was high enough to overcome the rotation potential barrier at a higher temperature so that the whole molecular chains were no longer forced to take a regular, periodic microconformation. This led to changes in the bond angle of the atoms in the lattice and the conformation, which made the macroconformation less ordered.
2. With the increase in the intersheet hydrogen-bond length, the long cycles of the crystal lattice in this direction decreased. This resulted in a reduction in the diffraction intensity.

From the WAXD diagrams, one can see that the crystals maintained a certain stability below 219°C and melted mainly in the range 221–231°C. This indicated that the α phase obtained by solution precipitation possessed better thermal stability; this was in accordance with the DSC results. Simultaneously, it also denoted that the whole melting process was due to the melting of the α phase.

Melting behavior and phase stability of LN-Ny6

Figures 2 and 5 show the DSC heating curve and HTWAXD patterns of LN-Ny6, respectively. There were three peaks on the DSC curve (Fig. 2), which were the cold crystallization peak, T_{m2} , and T_{m1} with a temperature range of 193–225°C. The WAXD results showed a sharp peak at $2\theta = 21.09^\circ$ at room temperature; this indicated that γ -phase crystals

were formed after quick quenching by liquid nitrogen and the reflection peak is related to the (100) (γ_1) reflection.

The cold crystallization peak with a range of 183–193°C on the DSC curve showed that the sample recrystallized during heating in this particular temperature range. The HTWAXD pattern shows that during heating, the peak shifted to a lower diffraction angle because of thermal expansion. Furthermore, the reflection intensity gradually increased, and the peak width at half-height decreased when the sample was heated below 180°C (Table III); this demonstrated that the γ -phase crystal developed slowly as the temperature increased below 180°C. The WAXD diagram of 180°C showed a small new crystalline shoulder peak at $2\theta = 20.15^\circ$. When the sample was heated to 200°C, another small peak was found at $2\theta = 22.29^\circ$; this suggested the formation of the α phase in the range 180–200°C. This corresponded very well with the recrystallization peak on the DSC curve.

With increasing temperature, the α_1 reflection shifted to a higher diffraction angle with a slight decrease in intensity. While the intensity decreased rapidly between 215 and 220°C. Slight evidence of α_1 ($2\theta = 20.46^\circ$) and α_2 ($2\theta = 22.45^\circ$) was shown on the WAXD pattern at 220°C; this means that the α -phase crystals formed under these conditions had different degrees of perfection and melted in the range 200–225°C. Accordingly, the γ_1 intensity decreased a little bit when the temperature reached 200°C, decreased remarkably from 215 to 220°C, and almost disappeared at 220°C; this showed that LN-Ny6 began to melt at 180–215°C but mainly melted at 215–220°C. As the temperature increased to 225°C, the pattern consisted of only one amorphous peak; this indicated that all the crystals melted completely.

When the samples were quenched in liquid nitrogen, the crystallization time was not long enough for sufficient motion of the segments and chains of nylon 6. The chains were frozen before they moved into the crystal lattice; this resulted in crystals with many more defects and that could rearrange and recrystallize more easily compared to Sol-Ny6. Consequently, a cold recrystallization peak was found on the DSC curve. What is more, the high-temperature α phase showed better thermal stability; it did not melt completely until 225°C. According to the results of WAXD, the lower melting peak with the range 193–210°C was deemed to be the melt of the low-perfection γ and α crystal, the higher melting peak at 219.6°C corresponded to the fusion of both the better perfection γ phase and the new crystalline high-temperature α phase forming at 183–193°C. The results show that the γ phase with better perfection melted mainly at a higher temperature, the same as the α phase of Sol-Ny6.

Melting behavior and phase stability of LNA-Ny6

When the quenched samples were annealed *in vacuo* at 190°C for 48 h, the LNA-Ny6 samples were obtained. Figure 3 shows the DSC heating curve of the sample; it showed very clearly double melting peaks at 219°C (T_{m1}) and 210°C (T_{m2}). As shown by the WAXD pattern of this sample at 25°C in Figure 6, there were two distinctive peaks at $2\theta = 20.08$ and 23.64° and a sharp peak at $2\theta = 21.32^\circ$ with a shoulder at $2\theta = 21.99^\circ$; this indicated the coexistence of the α and γ phases in this sample. As mentioned before, the former two peaks corresponded to α_1 and α_2 of the α -phase crystals; the latter ones corresponded to the hexagonal and pseudo-hexagonal packing structure resulting in the γ phase; these crystals are known as γ - and γ^* -phase crystals.^{19,25,26}

The HTWAXD patterns showed that the α -phase and γ^* -phase crystals formed during the annealing process were not stable upon heating. The two distinctive peaks at $2\theta = 20.08$ and 23.64° and the shoulder peak corresponding to γ^* phase ($2\theta = 21.99^\circ$) almost disappeared when the temperature reached 180°C, but the peak at $2\theta = 21.3^\circ$ became sharper, and the intensity increased dramatically with heating under 180°C. When the temperature reached 200°C, two new diffraction peaks at $2\theta = 20.35$ and 21.74° showed up as shoulders to the main peak; this indicated the formation of the high-temperature α phase, labeled as α_1' and α_2' , respectively, which was stable to 221°C. The diffraction peak of the γ phase at $2\theta = 21.3^\circ$ shifted to a lower diffraction angle with heating, and the intensity decreased to a certain extent in the temperature range 200–210°C and dropped sharply at 210–222°C. The WAXD pattern showed only one amorphous peak at 224°C; this suggested that all of the crystals were melted completely at this point.

Compared with the LN-Ny6 sample, the annealing processes did have a great effect on the crystalline structures of nylon 6. LN-Ny6 showed only γ -phase crystals at room temperature but formed α -phase and new γ^* -phase crystals after it was annealed at 190°C for 48 h. Meanwhile, the melting behaviors were totally different with the original quenched sample. From Figure 6, it is obvious that two structural transformation occurred when the sample was heated from room temperature to 200°C:

1. The pair of peaks at $2\theta = 20.08$ and 23.64° was replaced by a new pair of peaks at 20.35 and 21.74° . This indicated a structural transformation from one monoclinic lattice to a different crystalline (probably also monoclinic) lattice,²⁷ which were more thermally stable, as shown in the WAXD patterns.
2. The intensity of the peak at $2\theta = 21.99^\circ$ decreased, and the one at 21.3° increased. This

indicated that the γ^* -crystalline structure formed during annealing was easily changed into a more stable γ -phase structure, which melted at high temperature and did not transform into the α -phase crystals upon heating.

After they were annealed for 48 h, the crystals of the LN-Ny6 sample experienced a progress of improvement, with results in a series of different perfect degrees of crystals. Therefore, the fusion of the γ phase existed at both the lower and higher temperature, and part of the γ phase was more thermally stable, even more so than that of the high-temperature α phase.

When the results of DSC were compared with those of HTWAXD, there were no obvious caloric effect in the range 100–200°C on the DSC curves, but there were obvious melt recrystallization behaviors on the WAXD patterns, related to the structural transformation of the low-temperature α phase to the high-temperature α phase (α') and the γ^* phase to γ phase, as described previously. This may have been due to the canceling out of the heat absorption by melting behavior and heat release by recrystallization. T_{m2} at 210°C was mainly due to the melting behavior of the less perfect crystalline structure of the γ phase and a fraction of the α phase; T_{m1} at 219°C was due to the melting behavior of the high-temperature α - and γ -phase crystals with more perfect crystalline structures.

CONCLUSIONS

High-temperature X-ray diffraction and DSC were used to study the phase stability and melting behaviors of nylon 6. The results gave a very clear picture of the phase stability of the α - and γ -crystal structures and a more precise interpretation of the multi-melting peaks observed on the DSC curves.

The results show that most of the α phase obtained by the solution-precipitation process (Sol-Ny6) was thermodynamically stable, with T_{m1} at 221°C and double melting peaks on the DSC curve corresponding to the melting of α crystals with different degrees of crystal perfection. LN-Ny6 melted within 193–225°C, and the amorphous phase converted into the γ phase below 180°C but into the high-temperature α phase at 180–200°C. Both were stable over 220°C. The α -phase and γ^* -crystalline structures were formed by annealing *in vacuo* at 190°C for 48 h but were not so stable upon heating. Typical double melting peaks were shown on the DSC curve. Melt-recrystallization behavior occurred at 100–200°C; it corresponded to the crystal structure transformation of the low-temperature α phase to the high-temperature α crystalline phase (α') and the γ^* phase to the γ phase. The melting peak at 210°C was mainly due to

the melting behavior of the less perfect crystalline structure of the γ phase and a fraction of the α phase; the one at 219°C was mainly due to the melting behavior of the high-temperature α - and γ -phase crystals with more perfect crystalline structures.

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