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ORIGINAL CONTRIBUTION

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Influence of crystallization conditions on the crystalline transformation behavior of nylon 10 14

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Abstract Three kinds of nylon 10 14 crystals with different perfections were prepared under various crystallization conditions. The Brill transition behavior of these nylon 10 14 crystals was investigated by variable-temperature X-ray diffraction. It was found that the crystallization conditions influence the Brill transition temperature greatly. The Brill transition temperature of the lamellar crystals grown from dilute solution is so high that no Brill transition temperature can be observed before melting. However, for crystals postannealed at 125 °C, the Brill transition temperature is as low as 130 °C. The results show that the Brill transition behavior of nylons is strongly dependent on the crystallization conditions, for example, the perfections of the crystals.

Keywords Nylon 10 14 · Brill transition · Variable-temperature X-ray diffraction · Crystal perfection

Introduction

Most even–even nylons are α-form crystals at room temperature; this was initially proposed by Bunn and Garner [1] for nylon 66 and nylon 6 10. These triclinic structures consist of sheets of fully extended chains joined by hydrogen bonds and have two characteristic peaks in their X-ray diffractograms at room temperature. The *d* spacings are at about 0.37 and 0.44 nm, which correspond to the intersheet distance between the sheets and the projected interchain distance within the sheet, respectively. For some even–even nylons, the two diffraction peaks are found to converge on heating and finally merge into a single reflection at a certain temperature. This temperature is so-called the Brill transition temperature, T_B, which was first observed by Brill in 1942 [2].

Although there are many reports [3, 4, 5, 6, 7, 8] concerning the Brill transition behavior of nylons, the nature of this temperature-induced structural change is not fully understood. Early researchers [9, 10] suggested that the two-dimensional hydrogen-bonded sheets in the α form at room temperature are changed to a three-dimensional hydrogen-bonded network between the chains; therefore, the structure at high temperature has hexagonal symmetry. Some other workers [11] attributed the Brill transition process to nonisotropic thermal expansion of nylon crystals. Recently, some alternative models [12, 13, 14] have been proposed to explain the Brill transition of nylons; in these models the high-temperature crystals keep their triclinic structure with the hydrogen bonds arranged in sheets, but the projection along the *c*-axis has hexagonal symmetry because of the local melting of the methylene sequence between amide groups. Wunderlich and coworkers [15, 16, 17] found that the Brill transition is not a true first-order transition and the nylon crystals gradually become conformationally disordered mesophases below the melting temperature, T_m. Whatever models are preferred, it is commonly accepted that the nature of the Brill transition is considered to be the effect of conformational motion due to temperature and is associated with a packing change within the crystals [18].

Our previous studies on the Brill transition behavior of melt-crystallized nylon 10 10 [19], 10 12 [20, 21] and 12 12 [22] show that the T_B of these long-alkane-segment nylon samples are much lower compared with those of the solution-crystallized nylons which were carefully studied by Jones and coworkers [23, 24]. They stated that the T_B of solution-crystallized nylon 10 10, 10 12 and 12 12 are equal to or higher than their melting temperature, respectively. Then the obvious question arises: Does the Brill transition behavior strongly depend on the crystallization condition? Ramesh et al. [25] followed the isothermal crystallization process from the melt in nylon 66 in situ by X-ray diffraction and found that the transition always occurred about 40 °C below the crystallization temperature. However, the Brill transition behavior of different precrystallized nylon samples under different crystallization conditions has not been studied.

Nylon 10 14 is also a kind of long-alkane-segment nylon newly synthesized in our laboratory. The crystal structure has been reported in our previous work [26] and it crystallizes into the α form when crystallized from dilute solution. In this work, the crystalline transformation behavior of nylon 10 14 was studied carefully and the influence of the crystallization conditions on the T_B was also investigated.

Experimental

Material

Nylon 10 14 was synthesized by standard melt-polycondensation of 1,10-dodecanediamine and 1,12-dodecanedicarboxylic acid. The material used in this work had an intrinsic viscosity of 0.80 dl/g, which corresponds to a molecular weight of about 14,000 if the viscosimetric equation of nylon 66 is applied for the calculation.

Sample preparation

Solution crystallization sample

A solution of nylon 10 14 in 1,4-butanediol (0.05% w/v) was prepared. Crystals were grown isothermally at 135 °C for 36 h after seeding at 175 °C. The solution was hot-filtered at the crystallization temperature after the completion of crystallization. The sample was washed repeatedly with *n*-butanol and dried overnight in a vacuum oven at 80 °C. The mats obtained were cold-pressed to a rectangular sample with a thickness of about 1 mm for X-ray diffraction measurement.

Postannealed sample

The postannealed samples were prepared by pressing in a hot press at 200 °C and then quenching to room temperature in air. Then, te samples obtained were annealed at 125 and 160 °C for 24 h, respectively. The thickness of the sample is also about 1 mm.

Wide-angle X-ray diffraction

The wide-angle X-ray diffraction measurements were performed using a Rigaku III Dmax 2500 diffractometer with Cu radiation (35kV, 25 mA). The equipment was fitted with a high-temperature attachment. The sample was placed in a platinum block sample holder and was heated at 5 °C/min to the desired temperature and held there for 2 min before commencing the data collection.

Results and discussion

The wide-angle X-ray diffraction patterns of the three nylon 10 14 samples crystallized under different conditions are shown in Fig. 1. Curve A represents the X-ray diffractograms of lamellar crystals grown from dilute 1,4-butanediol solution. The X-ray diffraction patterns of postannealed samples at different temperature are also displayed in Fig. 1, as curves B and C, respectively. Two strong diffraction peaks can be seen in Fig. 1, which means that nylon 10 14 crystallized into the α form under these crystallization conditions. However, some differences can also be found as shown in Table 1.

It is generally accepted that the solution-crystallized sample has high crystallinity and a perfect crystal structure. This can also be observed from Fig. 1 and Table 1 because of the very strong and highly separated diffraction peaks. Nylon crystals quenched from melt and then postannealed show less perfection compared

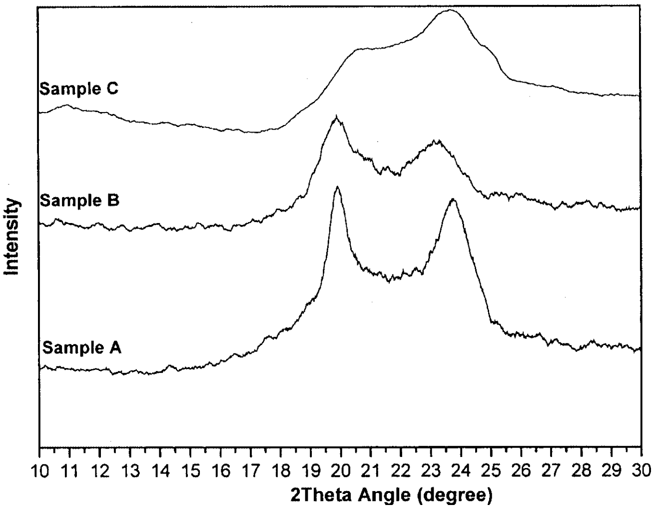

Fig. 1 X-ray diffraction patterns of nylon 10 14 samples crystallized under various conditions: *sample A* crystallized from dilute solution; *sample B* postannealed at 160 °C; *sample C* postannealed at 125 °C

Table 1 X-ray diffraction peaks and the *d* spacings of nylon 10 14 under different crystallization conditions. *vs*: very strong; *s*: strong

Sample	d_{100} spacing (nm)	$d_{010/110}$ spacing (nm)	d_{100}–$d_{010/110}$ (nm)
Sample A	0.446 (vs)	0.373 (vs)	0.073
Sample B	0.445 (vs)	0.376 (s)	0.069
Sample C	0.440 (s)	0.382 (s)	0.058

with that obtained from dilute solution. On decreasing the annealing temperature, the intensity of the reflections and the difference in the spacing between d_{100} and $d_{010/110}$ decrease, and the perfection of the crystals decreases accordingly. Therefore, we can conclude that the crystal of sample A has the highest perfection and that of sample C has the lowest crystal perfection.

The X-ray diffraction patterns taken as a function of temperature for the three samples are shown in Figs. 2, 3 and 4, respectively. The two strong reflections at room temperature, which are the characteristic projected interchain and intersheet diffraction signals, are found to converge slowly with increasing temperature. However, the transition behaviors of the three samples are very different. For sample A, the (100) and (010/110) spacings approach each other as the temperature increases. However, the melting takes place before the two spacings actually merge into one diffraction peak. This means that no T_{B} is achieved in the heating process. It has been reported that many long-alkane-segment nylons (nylon 8 10, 8 12, 10 10, 10 12, 12 12 and 6 18) crystallized from dilute solution show similar crystalline transition behavior [5, 6, 7].

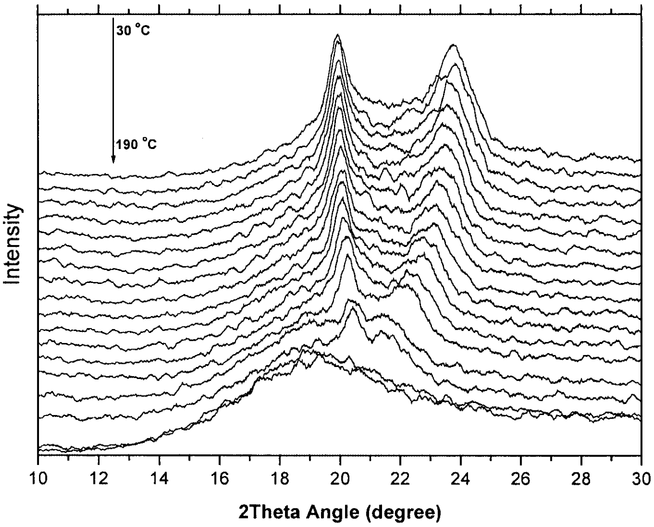

Fig. 2 X-ray diffraction patterns of nylon 10 14 crystallized from dilute solution obtained on heating from room temperature to melting

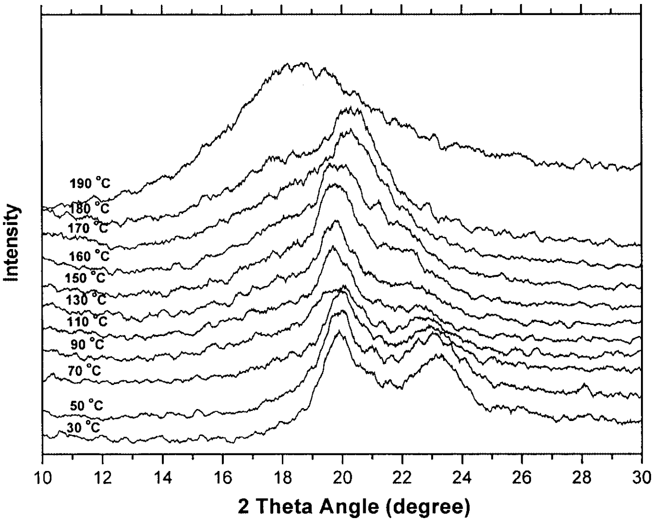

Fig. 3 X-ray diffraction patterns of nylon 10 14 postannealed at 160 °C obtained on heating from room temperature to melting

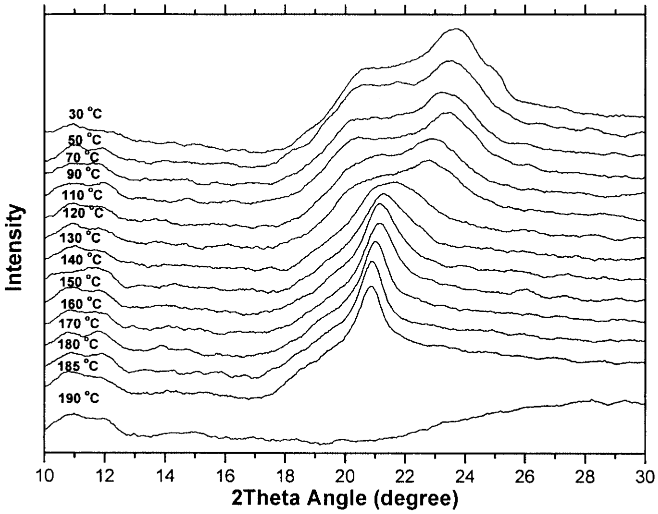

Fig. 4 X-ray diffraction patterns of nylon 10 14 post annealed at 125 °C obtained on heating from room temperature to melting

The Brill transition can be observed for samples B and C. The two strong reflections converge and merge into only one peak with increasing temperature. The transition behavior indicates the formation of the high-temperature pseudohexagonal modification. The changes in the spacings of the characteristic 100 and 010/110 diffraction signals for the three samples as a function of temperature are shown in Fig. 5. The 100 spacing of the three samples, i.e. the distance between 100 planes, is strongly fixed by the hydrogen bonds and hence is less sensitive to temperature variation. For samples B and C, $d_{010/110}$ has the same value as d_{100} at T_{B}, and the d spacing slightly increases owing to the normal thermal expansion above T_{B}. Although both samples B and C have a Brill transition before melting, their T_{B} are very different. The T_{B} of the sample annealed at 160 °C is as high as 170 °C but that of the sample annealed at 125 °C is only about 130 °C.

Although the nature of the Brill transition is not completely understood, modern measurement techniques, including NMR [27], Fourier transform IR [18, 21] and dynamic molecular simulation [28], show that the original hydroden bonds at room temperature remain without change before the melting on heating.

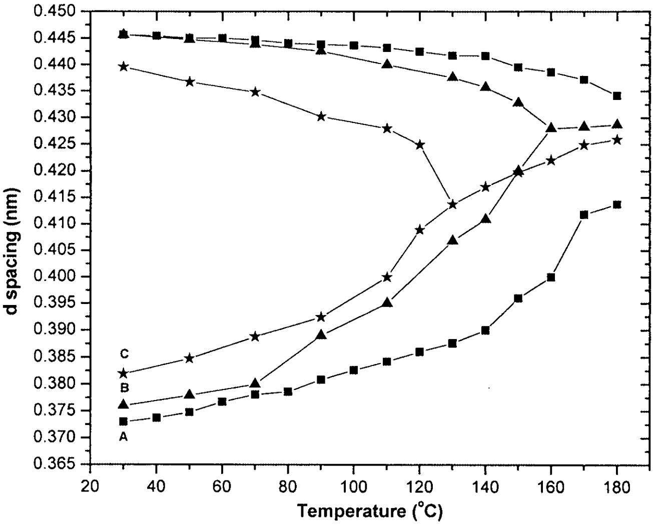

Fig. 5 Changes in the diffraction spacings of the three samples as a function of temperature: A Crystallized from dilute solution; *B* postannealed at 160 °C; *C* postannealed at 125 °C

That is to say, the Brill transition is caused by the local melting of methylene group between the hydrogen bonds, which are "anchors" and keep the crystal structure during heating. With increasing temperature, the mobility of the methylene sequence between the amide groups increases. At a certain temperature (T_B), the local melting of the methylene sequence takes place, so the projections of the crystal along the c-axis show the hexagonal symmetry and only one diffraction signal can be obtained. In fact, this hexagonal symmetry crystal is not the real hexagonal crystal but is the so-called "pseudohexagonal" form. It is well known that nylon crystals melt when the hydrogen bonds between the amide groups break down; therefore, both T_B and T_m decrease with increasing length of the alkane segments because of the decreasing hydrogen-bond density. However, T_m varies slightly with the change of the crystal perfections because almost all the amide groups are hydrogen bonded in nylon crystals with different perfections. In contrast, the conformation of the methylene sequence may be very different for the crystals crystallized under different crystallization conditions. For the crystals that crystallized from dilute solution, very perfect and regular crystals were obtained. The methylene sequence shows perfect zigzag conformations and the conformational change of the molecular chain is slow. As a long-alkane-segment nylon, the hydrogen-bond density of nylon 10 14 is low and the melting temperature is rather low. That is to say, the breakdown of hydrogen bonding takes place before the complete local melting of the long methylene sequence. Thus, no T_B can be obtained before melting. However, when we postannealed a quenched sample, the crystals obtained showed less perfection. Some methylene sequences between the "hydrogen-bond anchors" had not regulated to produce the perfect zigzag conformation, thus resulting in a lower diffraction intensity and a smaller difference between d_{100} and $d_{010/110}$. For these crystals, the methylene groups change their conformations easily and the crystals transform into the pseudohexagonal structure before melting during heating. Moreover, the perfection of the crystal increases with increasing annealing temperature and the T_B increases accordingly.

Conclusion

Different nylon 10 14 crystals with different perfection were obtained from various crystallization conditions. The Brill transition behavior of these crystals is also different: no T_B can be observed for the crystals grown from dilute solution before melting; the Brill transition takes place for the sample that was postannealed at different temperature. However, the T_B varies with a change of the postannealed temperature, the higher the postannealing temperature used, the higher the T_B that can be obtained.

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