Dependence of the Brill Transition on the Crystal Size of Nylon 10 10

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ABSTRACT: Nylon 10 10 crystals, which isothermally crystallized from the molten state and cold crystallized from melt-quenched samples at various temperatures, were investigated by using temperature-variable wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). No Brill transition occurred for the melt-crystallized crystals. However, this transition was easily observed for the cold-crystallized nylon 10 10, and the transition temperature is pertinent to the crystallization temperature. The sizes of these crystals was determined by SAXS and correlated with the Brill transition temperatures (T_B). It was found that the T_B had a linear relationship with the size of crystals, which was used to predict the T_B for those crystals with thick lamella and to calculate the crystal size showing T_B below room temperature. Nylon 10 10 crystal will possess the γ form (pseudohexagonal form) rather than the α phase at room temperature if its size becomes small enough.

Introduction

The Brill transition is a specific phenomenon observed in nylons, which was first reported by Brill[1] in 1942 on the investigation of X-ray diffraction of nylon 6 6. Since then, such a gradient and continuous transition has been observed in many nylons.[2−6] As a result, the crystal structure of nylons will transform into the pseudohexagonal phase from the triclinic or monoclinic form after reaching a temperature over the Brill transition temperature (T_B) for those crystals whose T_B values are lower than their melting point. Both melting point and Brill transition temperature are believed to decrease as the length of the alkyl segment in the nylon chains increases. Nevertheless, the rate of the depression of the Brill transition temperature is far slower than that of melting point. As a result, for those nylons with long alkyl segments in the repeating unit, the melt will take the place before the two predominant diffraction peaks on the wide-angle X-ray diffraction pattern completely merge into one diffraction signal during a continuous heating process. Additionally, the Brill transition is highly thermal-history-dependent.[7−9] Even for otherwise identical nylon samples resulting from different thermal histories, great differences in the T_B can be observed.

Nylon 10 10 is another member in the family of 2*N* 2*N* serial nylons. There are more hydrocarbon units in both the diacid and diaminoalkyl segments than that in nylon 6 6. Consequently, nylon 10 10 features a higher dimensional stability and a lower moisture absorption than nylon 6 6 does. The melting point of nylon 10 10 is ca. 202 °C, which is much lower than that of nylon 6 6 which is as high as 260 °C. The Brill transition cannot be observed during the heating process for those melt-crystallized or solution-grown nylon 10 10 crystals. However, this transition can be clearly observed for the cold-crystallized specimens, and their transition temperatures are greatly dependent on the crystallization temperature.

Commonly, cold crystallization from an amorphous state at different temperatures results in crystals with different lamellar thicknesses. Is there any relationship between the lamellar thickness and T_B? The effect of crystal size on the phase transition temperature is observed in several polymers.[10,11] The crystallization of polyethylene at elevated pressure results in the extended-chain crystals[12−14] that show high symmetry in two dimensions and belong to hexagonal form. Obviously, the hexagonal structure of PE is the consequence of large lamellar thickness in its crystals. The crystal-to-crystal transition of *trans*-1,4-polybutadiene from monoclinic to hexagonal phase or reverse is also dependent on its size (lamellar thickness).[15,16]

In this article, we studied the Brill transition of nylon 10 10 cold-crystallized from the melt-quenched state. The lamellar thickness and long period in these samples were determined by using small-angle X-ray scattering (SAXS). A quantitative relationship between the T_B and the crystal size was obtained. T_B values of those melt-crystallized nylon 10 10 and sizes of crystals showing the γ form at room temperature were determined.

Experimental Section

The nylon 10 10 used in this work was a granular commercial product of the Shanghai Cellulose Works, Shanghai, China. The sample was intensively purified before use.

The specimen for X-ray diffraction analysis was prepared as follows: the purified powder sample was pressed between thin aluminum foil and heated to 250 °C, kept for 5 min at this temperature, and then the sample was quenched in liquid nitrogen as quickly as possible. Afterward, the obtained quenched sample was isothermally crystallized (cold crystallization) at various temperatures. All the heating and crystallization operations were conducted in an environment filled with oxygen-free dried nitrogen.

Wide-Angle X-ray Diffraction. Wide-angle X-ray diffraction (WAXD) measurements of the crystallized samples were carried out by using a Philips PW-1700 mode automatic X-ray diffractometer equipped with a specially designed temperature-controlled chamber which allows a maximum heating and cooling rate of 10 °C/min. Ni-filtered Cu Kα radiation from a generator operating at 40 kV and 30 mA was used in the experiment. The chamber temperature was calibrated by the melting point of tin (232 °C) and the transition point of potassium nitrate (130 °C). A step of 0.02° was used in all scans from 5 to 35°.

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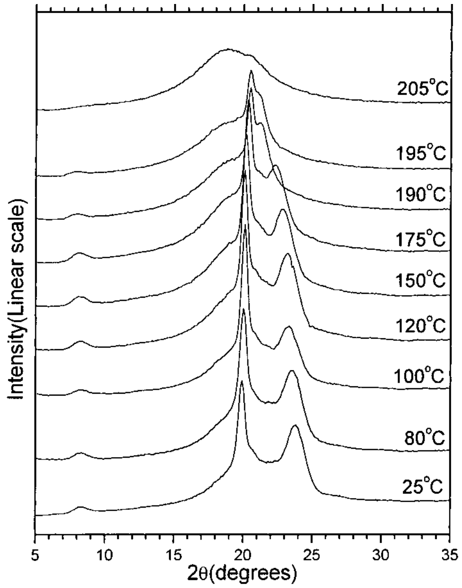

Figure 1. Series of WAXD profiles in a continuous heating process for the isothermally melt-crystallized nylon 10 10 at 180 °C for 24 h.

Small-Angle X-ray Scattering. SAXS intensities for the nylon 10 10 samples were obtained on the same X-ray apparatus, equipped with a Kratky small-angle X-ray camera and a sample-to-detector distance of 200 mm. The measurements were performed with a Cu Kα radiation source operated at 60 kV and 30 mA. The scattering intensities were corrected for absorption, background scattering, and incident X-ray fluctuations of the samples. A desmearing procedure developed by Schmidt[17] was introduced to correct the scattering intensities. The resulting intensities were converted to the absolute scattering intensity using a calibrated Lupolen (Polythelene BASF, Ludwigshafen, Germany) standard sample.[18] A one-dimensional electron density correlation function (EDCF) was obtained based on the corrected SAXS intensities and was used to determine the long period and lamellar thickness.[19]

DSC Measurements. Thermograms of the samples were obtained with a Perkin-Elmer 7 series thermal analysis system operated in standard DSC mode on approximately 10 mg samples at a scanning rate of 10 °C /min. The temperature and heat of melting were calibrated with a high-purity indium standard. A nitrogen purge was provided throughout the DSC scan.

Deconvolution Procedure. The peaks of interest were relatively close together in the transition region. Therefore, the position of the (010/110) doublet reflection could only be fixed by deconvoluting the (100) and (010/110) peaks. The diffraction profiles were assumed to be composed of three peaks: two crystalline peaks from (100) and (010/110) diffraction, respectively, and an amorphous peak. It was almost impossible to obtain the completely amorphous peak by quenching nylon 10 10 from its molten state. Therefore, the amorphous peak position was fixed by extrapolating the amorphous peak positions near the melting point during the heating process. For measurement of the dependence of the structure of the α phase on the temperature, lamellar crystals[20] with high crystallinity, which were isothermally crystallized from very dilute DMF solution, were used.

Results

A series of WAXD profiles for the melt-crystallized nylon 10 10 measured in a continuous heating process are shown in Figure 1. The (100) and (010/110) doublet diffraction peaks gradually approached each other as the temperature increased but never merged into one before melting. This gave the proof that no real Brill transition occurred in this sample.

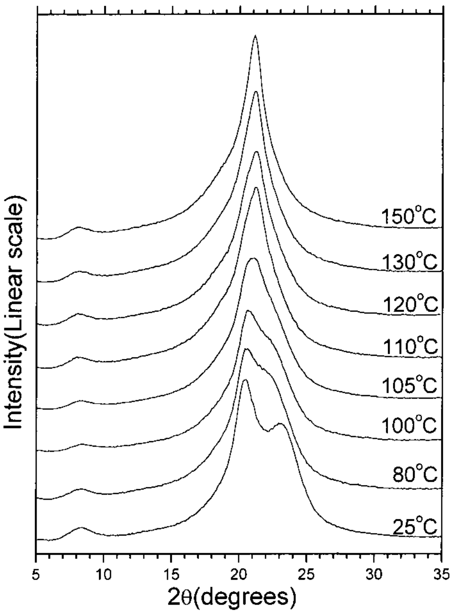

Figure 2. Characteristic WAXD profiles in a continuous heating process for the cold-crystallized nylon 10 10 (what shown in this figure is the sample crystallized at 120 °C for 24 h).

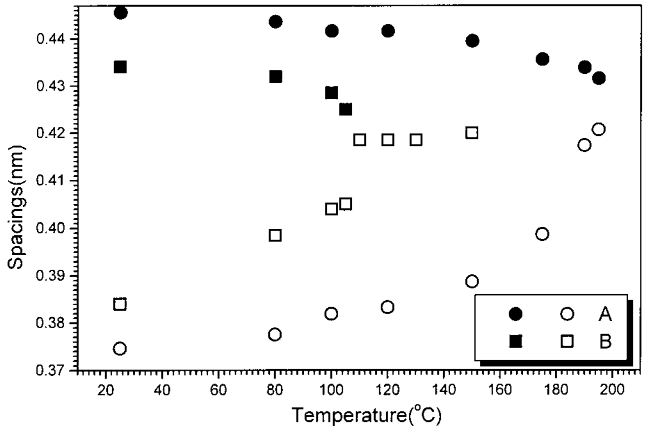

Figure 3. Comparison of the variation of *d*-spacings on the continuous heating for (A) melt-crystallized and (B) cold-crystallized nylon 10 10.

Figure 2 gives the WAXD diffractograms of cold-crystallized sample during continuous heating. Here only the profiles of the sample cold-crystallized at 120 °C for 24 h are illustrated. The main diffraction peaks approached each other with the increase in temperature and merged into one single reflection at 110 °C. The pseudohexagonal phase (γ form) of nylon 10 10 was thus obtained after the temperature was increased over this value.

The variations of *d*-spacings with temperature in heating process between the melt-crystallized and cold-crystallized samples are compared and shown in Figure 3. In the melt-crystallized nylon 10 10, there was a continuous change of the *d*-spacings. However, even when the temperature was close to the melting point, (100) and (010)/(110) still separated from each other. In contrast, the two main diffraction peaks merged into one single reflection at a quite a bit lower temperature for the cold-crystallized sample. Therefore, the γ form of nylon 10 10 can be easily achieved in those cold-crystallized samples as compared to melt-crystallized specimens.

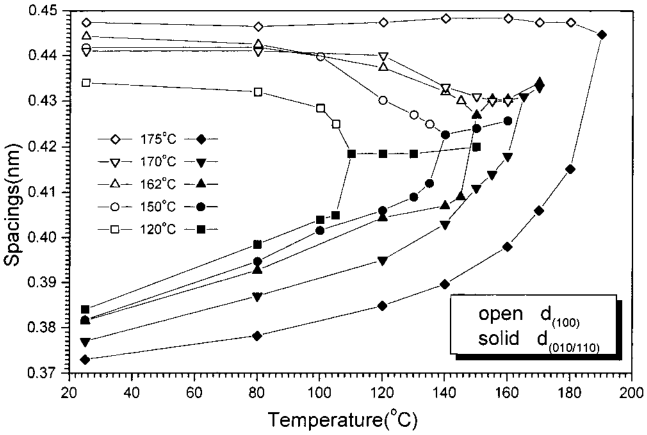

Figure 4. Variation of two main *d*-spacings as a function of temperature for the nylon 10 10 crystals cold-crystallized at different temperatures for 24 h.

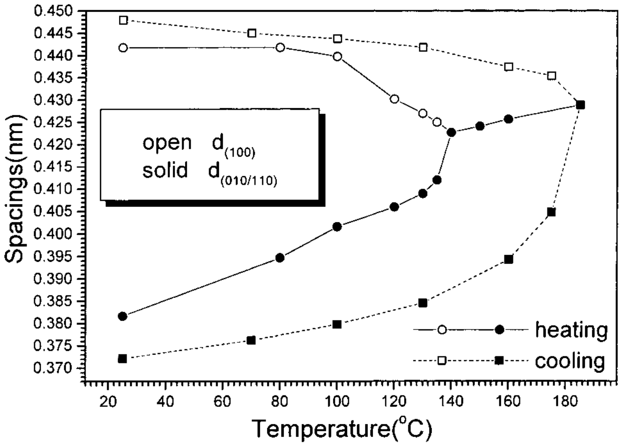

Figure 5. Comparison of the variation of *d* spacings with temperature between heating and cooling process for the cold-crystallized (at 150 °C for 24 h) nylon 10 10.

The characteristic feature of the Brill transition for the cold-crystallized nylon 10 10 was described above. Then, for the crystals with such a thermal history, how the crystallization temperature affects the transition temperature becomes an urgent problem. The variations of *d*-spacings as a function of temperature during continuous heating process for those nylon 10 10 cold-crystallized at various temperatures are shown in Figure 4. The two diffraction peaks of all the samples merged into one diffraction maximum at a temperature around their respective crystallization temperatures. After that, the spacings became slightly enlarged during the following heating process because of general thermal expansion. The complete merging of the two peaks indicates that the Brill transition temperature occurred and that the crystal phase of nylon 10 10 was thus transformed from the α form into the γ form.

It is of interest to compare the continuous change of *d*-spacings between the heating and cooling process. For the cold-crystallized samples, the variation of spacings with temperature from the triclinic to the pseudohexagonal structure on heating was different from the reverse transition during the cooling process. The variations of *d*-spacings with temperature between heating and cooling processes are compared and shown in Figure 5. The nylon 10 10 sample, which was cold-crystallized at 150 °C for 24 h, was continuously heated from room temperature to 185 °C, kept for 1 h at this temperature, then cooled to room temperature with a rate of 10 °C/min. On the cooling process, the (100) and (010)/(110) reflections immediately separated from each other as soon as the temperature dropped from the highest temperature exerted on the sample. This indicates that the cooling of the heated crystal at 185 °C resulted in the transition of nylon 10 10 from the pseudohexagonal phase to the triclinic form. At room temperature, the discrepancy of d_{100} and $d_{010/110}$ for sample heated to 185 °C was greater than that of the original sample. The difference of spacing variations between heating and cooling process prompts the theory that either melt-quenched or cold-crystallized nylon 10 10 crystals can well memorize the highest temperature exerted on it. This is a characteristic feature of nylon crystals, which is observed in the other members.[2,21]

Analysis of long period and lamellar thickness for the samples was based upon the one-dimensional electron density correlation function.[19] This function is related to the electron density variation $\eta(Z)$ along the lamellar normal if this variation obeys a "linear model", i.e., the density variations mainly occur along the direction perpendicular to the lamellae. Therefore, the correlation function $K(Z)$ can be written as

$$K(Z) = \langle \eta(Z') \rangle - \langle \eta \rangle [\eta(Z + Z') - \langle \eta \rangle] \rangle \qquad (1)$$

where Z is the direction normal to lamellar stacks; angular brackets indicate averaging over all coordinates Z' within a stack; the average electron density within the stack is represented by $\langle \eta \rangle$; and $K(Z)$ can be obtained by Fourier transformation of the desmeared scattering curve

$$K(Z) = \int_0^\infty 4\pi s^2 I(s) \cos(2\pi s Z)\, \mathrm{d}s \qquad (2)$$

where s, denotes the reciprocal space coordinate and $s = 2(\sin\theta)/\lambda$, θ is the Bragg angle, and λ is the X-ray wavelength.

The long period and lamellar thickness of the samples cold-crystallized at different temperatures were determined by the one-dimensional electrodensity correlation function (EDCF). The interphase[22] between crystalline and amorphous layers was considered in the calculation of the lamellar thickness. The SAXS intensities and EDCF curves for both cold-crystallized and melt-crystallized nylon 10 10 are shown in Figures 6 and 7, respectively. The lamellar thickness of the cold-crystallized nylon 10 10 was rather low due to the difficulty of movement of the polymer segment from the melt-quenched state to regular packing with three-dimensional order. Therefore, the relative crystallinity of these samples was rather lower than that of melt-crystallized nylon 10 10 (The detailed data are shown in Table 1). However, both lamellar thickness and long period obviously increased with the cold crystallization temperature. The Brill transition temperature, long period, lamellar thickness, and relative crystallinity of the cold-crystallized samples at different temperatures as well as melt-crystallized samples of nylon 10 10 are shown in Table 1. The crystallinity was determined from DSC by using ΔH_{m} on the heating process and $\Delta H_{\mathrm{m}}^0 = 244.0$ J/g of nylon 10 10.[23] Due to the effect of the interphase on the average lamellar thickness, the crystallinity calculated from d/L is always higher than the DSC crystallinity for the cold-crystallized samples.

Table 1. Brill Transition Temperature, Lamellar Thickness, Long Period, and Crystallinity for Nylon 10 10

cold crystallization temp (°C)	Brill transition temp (°C)	av lamellar thickness (including interphase) (Å)	long period (Å)	*d*/*L*	DSC crystallinity (%)
120	110	28.0	69.5	0.403	29.9
150	140	33.0	77.6	0.425	35.2
162	150	35.0	82.5	0.424	36.9
170	165	37.9	89.0	0.426	38.1
175	190	41.0	96.3	0.426	38.9
melt-crystallized	no	45.6	103.9	0.438	43.9

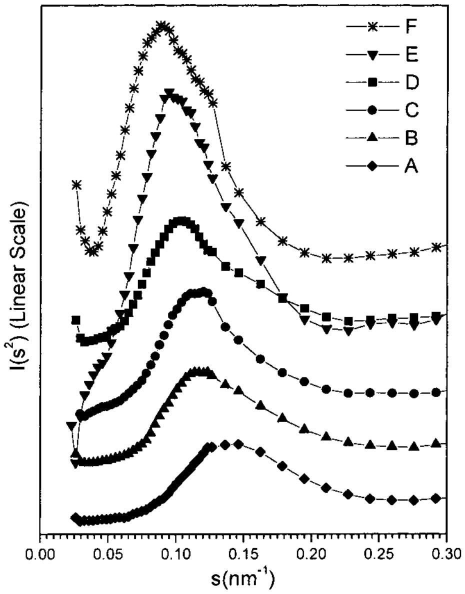

Figure 6. Desmeared and Lorentz corrected SAXS intensities for the cold-crystallized nylon 10 10 at (A) 120, (B) 150, (C) 162, (D) 170, and (E) 175 °C for 24 h and (F) melted and isothermally crystallized nylon 10 10 at 180 °C for 24 h.

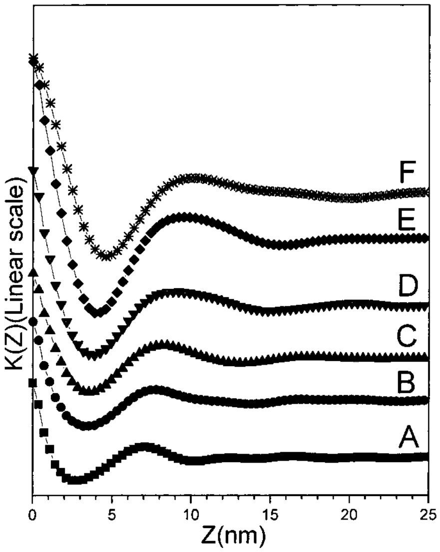

Figure 7. One-dimensional electrodensity correlation function (EDCF) for the nylon 10 10 crystal with the same thermal history as shown in Figure 6.

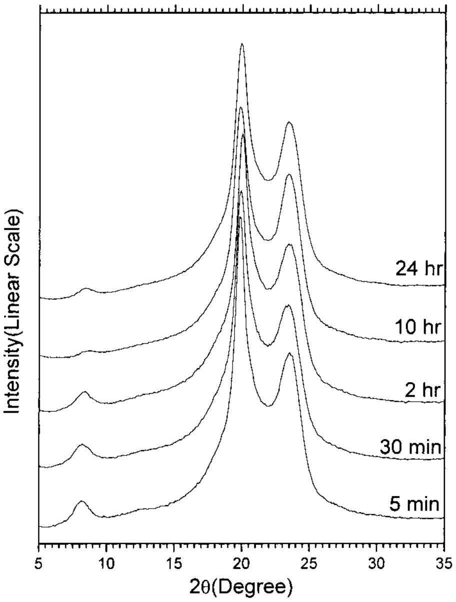

Figure 8. WAXD profiles for the melt-quenched nylon 10 10 following postannealing at 170 °C for different times.

It is well-known that the lamellar thickness of a semicrystalline polymer is dependent on its thermal history. Melt crystallization can generate crystals with relatively thick lamellae and wide size distribution. That is to say it is rather difficult to obtain the small size crystals with certain lamellar thicknesses by using melt crystallization. However, for cold crystallization from the glass state, it is easy to control the crystal size. The final crystal thickness is dependent on the crystallization temperature. What is shown in Figures 6 and 7 vividly gives the long periods and different lamellar thickness of nylon 10 10 crystals obtained from different crystallization temperatures but with the same crystallization time.

It is reported that continuously annealing the melt-crystallized nylon 11 at a fixed temperature results in lamellar thickening.[24] However, for those solution precipitated crystal mats, the first effect of annealing is a small reduction of the long period. Some authors report that annealing some polyamides other than nylon 6 6 results in little or no change at all.[25]

To investigate the effect of annealing time on the crystal size of nylon 10 10, the melt-quenched sample was annealed[26] at 170 °C for from 5 min to 24 h. The WAXD profiles measured at room temperature for variously annealed nylon 10 10 samples are shown in Figure 8. All the diffraction peaks were almost at the same position irrespective of the different annealing times. In addition, the long period and lamellar thickness were independent of the annealing time, which can be proved by the Lorentz SAXS intensity and one-dimensional electrodensity function as shown in Figures 9 and 10, respectively.

Discussion

The dependence of transition temperature on the lamellar thickness (commonly called size) of crystals has been reported for some crystalline polymers.[12−15,27,28] The hexagonal phase of PE developed under high

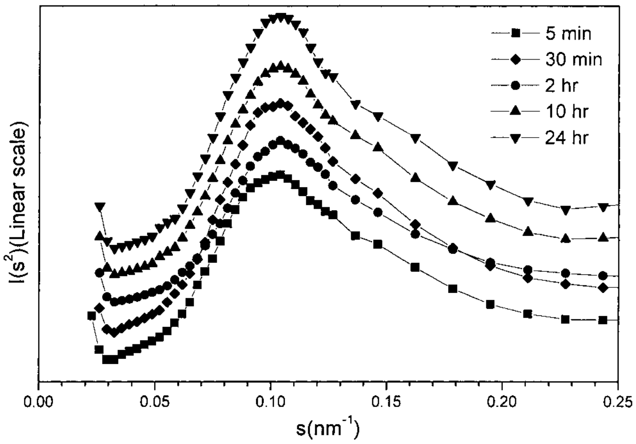

Figure 9. Desmeared and Lorentz corrected SAXS intensities for the nylon 10 10 crystals with the same history as shown in Figure 8.

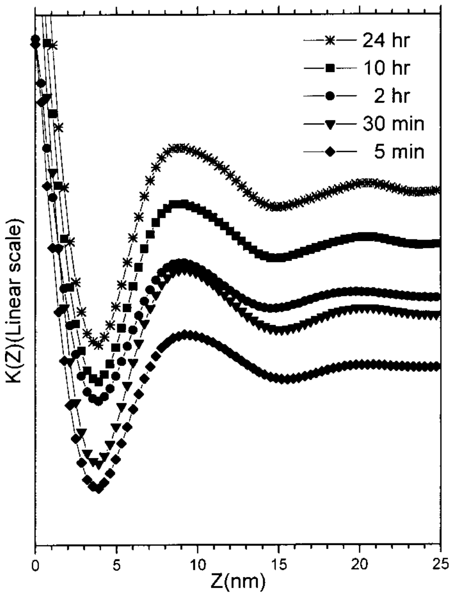

Figure 10. One-dimensional electrodensity correlation function (EDCF) for the nylon 10 10 crystals derived from the SAXS intensities as shown in Figure 9.

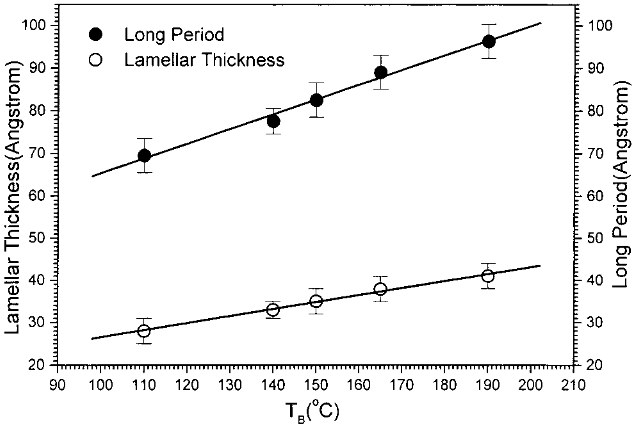

Figure 11. Dependence of the Brill transition temperature on the lamellar thickness and long period of the crystals for the cold-crystallized nylon 10 10.

pressure is attributed to the size effect.[12-14] Another predominant example is the crystal-to-crystal transition of *trans*-1,4-polybutadiene. The time-resolved synchrotron wide-angle X-ray diffraction for *trans*-1,4-polybutadiene obtained during heating and annealing processes gives proof that the size of the crystals determines the transition.[15] Both the single-chain single crystal and pauci-chain single-crystal developed in gutta-percha[27,28] possess different crystal structures from its bulk structure, which gives proof that the size of the gutta-percha crystals affects its crystal structure. All the experimental results prove that the size does affect the stability of the specific crystal form of a polymer, and as a result, it would change the phase transition temperature.

The Brill transition is a reversible transition for those well-crystallized nylon crystals. The transition from triclinic form to pseudohexagonal phase can be observed during the continuous heating process and reverse transition on cooling. For the nylons whose Brill transition temperatures are much lower than their melting points, such as nylon 6 6, their Brill transition temperature can always be observed irrespective of the various crystallization conditions. However, the transition temperature always varies with different thermal histories.

Some workers[29] propose that the Brill transition temperature is probably pertinent to the size and perfection of the crystals on investigation of the crystalline phase of nylon 6 6 by solid-state ^{2}H NMR. However, no any further results regarding this for a nylon polymer can be found in the literature, even for the qualitative relationship between T_B and size. The Brill transition temperatures of cold-crystallized nylon 10 10 crystals were correlated with their sizes. Shown in Figure 11 is the dependence of T_B on lamellar thickness and long period of crystals. We found that all the dots, which represent the relationships between the T_B and lamellar thickness or T_B and long period, could be fitted with the respective linear relations. As a result, the quantitative relationships between T_B and long period, T_B and lamellar thickness were obtained. Equations 3 and 4 give such relations, in which d represents the average lamellar thickness and L is the long period of crystals.

$$d = 10.27 + 0.1626T_B \tag{3}$$

$$L = 30.81 + 0.3455T_B \tag{4}$$

Having obtained the relationships between T_B and lamellar thickness and between T_B and long period, we can calculate the T_B values for those melt-crystallized or solution-grown crystals. These crystals have a great tendency to inhabit thick lamellae and, therefore, their T_B values will be higher than the melting temperature. For melt and isothermally crystallized (at 180 °C) nylon 10 10, its long period and lamellar thickness determined from EDCF based on SAXS intensities were 103.9 and 45.6 Å, respectively. By using this lamellar thickness and long period as well as their relationships with T_B, the Brill transition temperatures of these crystals were extrapolated to be 212 and 215 °C, respectively. The T_B values calculated from the extrapolation of lamellar thickness and long period were very close. However, both of them were higher than the melting point of nylon 10 10. Therefore, the real Brill transition has never been observed in both the melt-crystallized and solution-grown nylon 10 10 crystals. However, if these two linear functions are extrapolated to room temperature, one can obtain the size of the nylon 10 10 crystals which have the Brill transition at room temperature (25 °C). These crystals should have lamellar thickness and

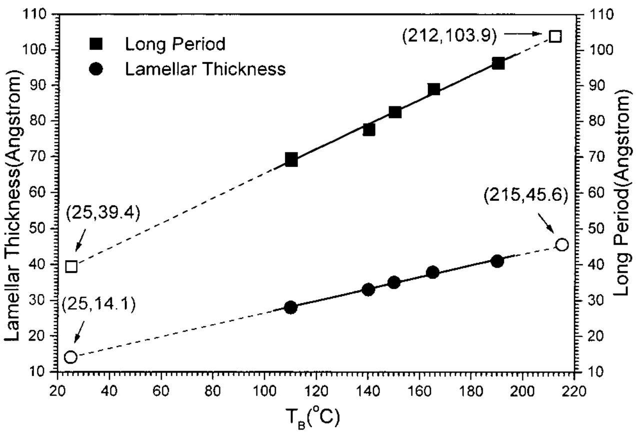

Figure 12. Determination of Brill transition temperature for thick lamellae and prediction of the lamellar thickness and long period for the crystals with the γ form at room temperature by using the linear functions as shown in Figure 11.

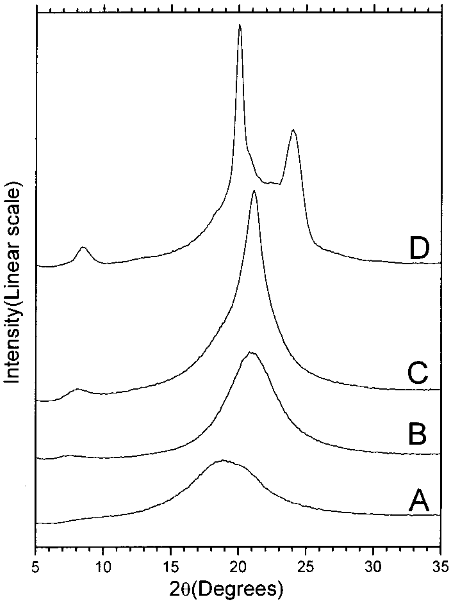

Figure 13. WAXD profiles of nylon 10 10 in various forms: (A) molten state measured at 220 °C; (B) melt-quenched state measured at room temperature; (C) cold-crystallized state measured at a temperature well above its Brill transition point; (D) melt-crystallized state measured at room temperature.

long period as small as 14.1 and 39.4 Å, respectively. All the extrapolations and calculations are schematically represented in Figure 12. From these results, it is conceivable that nylon 10 10 will show the γ phase (pseudohexagonal form) at room temperature when its size is small enough. For the melt-quenched nylon 10 10 sample, it always gave a broad peak with spacing of 0.42 nm, which is different from the amorphous halo. The WAXD diffractograms for the molten, melt-quenched nylon 10 10, the pseudohexagonal sample obtained by heating cold-crystallized nylon 10 10 well over its crystallization temperature, and the melt-crystallized triclinic form of nylon 10 10 were compared and shown in Figure 13. The position of the predominant diffraction peak for the melt-quenched sample was the same as that for the pseudohexagonal form even though its profile was much wider. The analogous WAXD diffractogram between the γ form and quenched nylon 10 10 indicates that the polymer stems in quenched sample must inhabit some regular packing to a certain extent. However, the length of the continuous packing period should be especially short. If we regard these packing orders as crystal or pseudo-crystal, the size was also small. Consequently, the quenched sample showed a pseudohexagonal structure even at room temperature.

Despite many related works, a complete understanding of the Brill transition does not exist. Many possible mechanisms are proposed for interpreting this characteristic and interesting transition. Brill[1] and co-workers propose that the transition from the triclinic or monoclinic form to the pseudohexagonal structure be the result of breaking and re-forming of the hydrogen bonds from the original hydrogen-bonded sheet structure to a three-dimensional hydrogen bond cross-linking network.[9,30] However, this viewpoint has been argued against by a number of authors.[2,3,29] On the contrary, they believe that the original hydrogen bonds remained without change before the melting. Some workers[2,3,29,31,32] propose that the Brill transition is not a true, first-order phase transition. The variation of d-spacings is the result of thermal disorder of alkylene segment on the nylon chains. The Brill transition indicates the start of a great motion of alkylene groups. However, due to the strong action of these hydrocarbon segments, the variation of spacings within hydrogen-bonded sheets is especially difficult. Therefore, the change in the a-axis is limited. However, another question arose, due to the stable structure of hydrogen bonds, where the expansion of intersheet spacing along the b-axis can only be carried out through the movement of the integrated hydrogen-bonded sheets. For this reason, it is clear that the spacing expansion will be affected by the size of the sheets. For the cold-crystallized crystals from the melt-quenched state, the crystal size is strongly dependent on the crystallization temperature. We believe the d-spacings of nylon crystal during the Brill transition is the result of the balance between the thermal motion and packing tendency of polymer stems within crystals. For large crystals, a great tendency for the crystal to maintain its original stable packing order is observed. Therefore, a higher temperature is necessary to break such a balance. On the other hand, the packing order of a small crystal is easily destroyed by the motion of polymer stems even at a rather low temperature. The small size of the hydrogen-bonded sheets resulted in weak action between the sheets and thus an easy movement of sheets during thermal expansion as the temperature increased. Therefore, the smaller the crystal size is, the lower the Brill transition temperature occurs. For the melt-crystallized spherulites or solution-grown lamellar crystals, their size was larger than the critical size of nylon 10 10 needed to show T_B. It is definite that no real Brill transition was achieved. In contrast, for a crystal with an especially small size, such as some “crystals” in the quenched nylon 10 10, T_B was lower than room temperature. Therefore, the crystal exhibits a pseudohexagonal form (γ form) even at room temperature.

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(26) As shown in Figure 13, the melt-quenched sample is not in a truly amorphous state. There is still some regular packing between the polymeric chains. Nylon 10 10 with such a thermal history can be regarded as a kind of crystal with two-dimensional structure. Therefore, here we used “annealing” instead of “cold-crystallization”.
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