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ORIGINAL CONTRIBUTION

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In situ Fourier transform IR spectroscopy and variable-temperature wide-angle X-ray diffraction studies on the crystalline transformation of melt-crystallized nylon 12 12

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Abstract The crystalline transformation in nylon 12 12 was monitored by variable-temperature wide-angle X-ray diffraction during heating, isothermal and cooling processes. It could be found that the α phase of the sample transforms into a γ phase at about 130 °C if the sample is heated from room temperature to a high temperature, which is the so-called Brill transition temperature. In addition, nylon 12 12 was found to crystallize into the γ phase when isothermally crystallized at high temperature from the melt. Upon further cooling from the crystallization temperature to room temperature, the reverse transition from the γ phase to the α phase can be detected. Furthermore, in situ Fourier transform IR spectroscopy was also used to study the Brill transition of nylon 12 12 samples on both heating and cooling. It is interesting that the hydrogen-bond strength in nylons decreases dramatically and that some Brill bands of nylon 12 12 disappear abruptly during the Brill transition on heating.

Keywords Nylon 12 12 · Brill transition · Variable-temperature wide-angle X-ray diffraction · In situ Fourier transform IR spectroscopy

Introduction

A number of nylons show a crystal-to-crystal transformation on heating, which is known as the Brill transition. This phenomenon was observed first in nylon 66 by Brill [1]. In recent years, it has been found that many even–even nylons and even nylons can also display a Brill transition [2–9]; however, the mechanism of the transition is not fully understood. Two models were proposed to explain the transformation process. Early researchers [10–12] suggested that the two-dimensional hydrogen-bonded sheets in the α form at room temperature change to a three-dimensional hydrogen-bonded network between chains at high temperature. Some other workers [13, 14] thought that the polymer at high temperature keeps the α form with hydrogen bonds arranged in sheets, but the projection along the *c*-axis has hexagonal symmetry. Whatever models are preferable, it is commonly accepted that the origin of the Brill transition is the effect of conformational motion owing to the increase in temperature and it is associated with a packing change within the crystal [1, 15, 16].

Usually, the Brill transition is most clearly displayed by wide-angle X-ray diffraction (WAXD) [17, 18]. On heating polyamides, the two strong diffraction signals with spacings of 0.44 and 0.37 nm (100 and 010/110 reflections) are observed to move together and meet typically at a spacing of 0.42 nm. The "Brill temperature" (T_B) is defined as the lowest temperature when the projected interchain distance within hydrogen-bonded sheets equals to the intersheet spacing. That is to say, the room temperature triclinic structure transforms into a pseudohexagonal structure during the Brill transition. Other techniques, such as differential scanning calorimetry [19], NMR [14] and small-angle X-ray scattering [20], have also been used to detect the Brill transition. Unfortunately, most of them are not very sensitive to the transition. Recently, variable-temperature IR spectroscopy was used by Vasanthan et al. [15] to examine the Brill transition in nylon 6 and nylon 66. The authors identified some "Brill bands" which can be used to detect the Brill transition of nylons; however, they also stated that no significant changes were observed in the hydrogen bonding during the Brill transition.

Nylon 12 12 is an important industrial polyamide with rather long alkane segments between amide groups and it has a relatively low melting point compared with other nylons. Jones et al. [5] studied the Brill transition behavior of solution-crystallized nylon 12 12 and found that the T_B of the solution-crystallized sample is equal to its melting temperature. It is well known that the T_B is not only determined by the structure of the nylons, but also strongly depends on the crystallization conditions [18]. No attention has been paid to the crystalline transitions of melt-crystallized nylon 12 12 hitherto. In this work, Variable-temperature WAXD and in situ Fourier transform IR (FTIR) spectroscopy were used to investigate the Brill transition behavior of melt-crystallized nylon 12 12. The evident decrease in the strength of the hydrogen bonds during the Brill transition was detected by in situ FTIR spectroscopy.

Experimental

Sample preparation

The samples of nylon 12 12 free of additive were kindly provided by Genius New Materials Company with a relative viscosity of 1.88 measured in 96% H_2SO_4, 10 gl^{-1}. Films of nylon 12 12 about 20-μm thick for the IR measurements were pressed between two glass slides at 200 °C on a hot stage, then annealed in an oven at 120 °C for 5 h. Thick samples for the WAXD measurements were produced using the same procedure.

Wide-angle X-ray diffraction

WAXD 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/cooled at 5 °C min^{-1} to the desired temperature and held there for 2 min before commencing the data collection.

In situ IR spectroscopy

The IR spectra were collected at a resolution of 4 cm^{-1} using a Bruker Equinox-55 FTIR spectrometer equipped with a variable-temperature cell. The sample was heated from room temperature to 200 °C at 5 °C min^{-1}. At the same time, FTIR spectra were recorded at a rate of 1 spectrum each 30 s. Sets of eight scans were used for signal averaging. A curve-fitting procedure with the Lorentzian method was used to resolve selected IR bands and determine the area under the peaks.

Results

WAXD measurements

The development of the WAXD pattern during heating the sample of nylon 12 12 is shown in Fig. 1. It can be seen from Fig. 1 that the pattern has teo peaks, at $2\theta = 20.2°$ and $2\theta = 23.3°$, at room temperature. The d spacings corresponding to the two crystalline peaks are 0.438 and 0.381 nm, respectively, which represent the projected interchain distance within a hydrogen-bonded sheet and the intersheet distance, respectively. The intersheet distance is a little larger than the theoretical

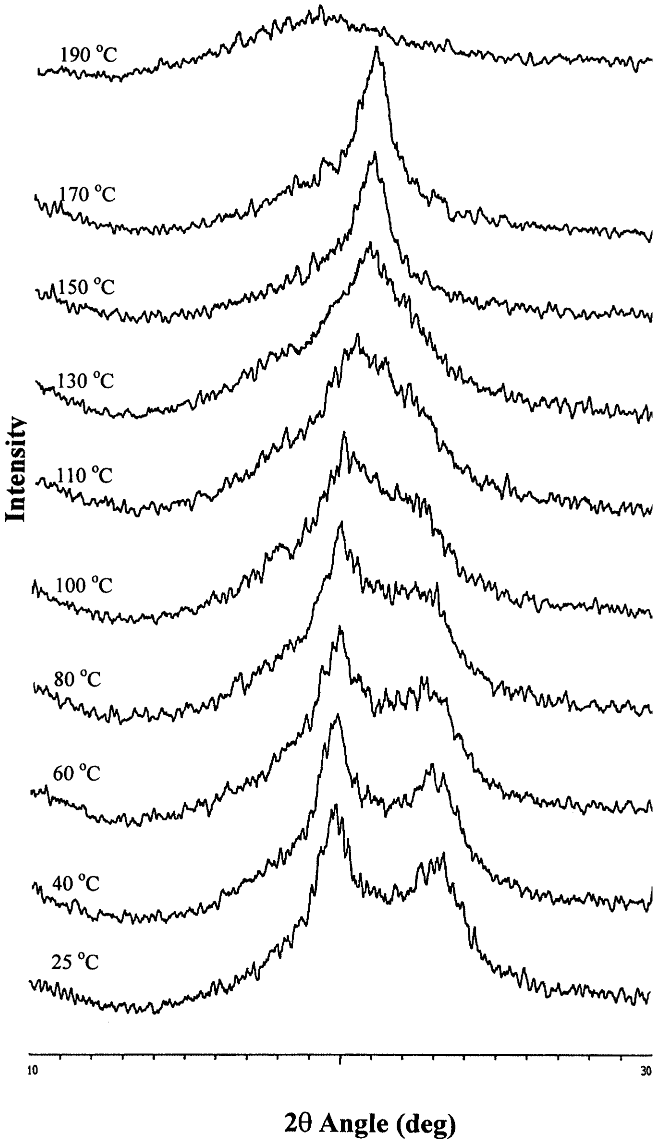

Fig. 1 X-ray diffraction patterns of nylon 12 12 obtained on heating from room temperature to melting

value (0.37 nm), which may result from the long alkane segments of nylon 12 12 and the crystallization conditions used in this work. The two reflections are characteristic of the α form of nylon 12 12. With increasing temperature, the two reflections converge and merge into one peak at 130 °C, which is the so-called Brill temperature. The variation of the *d* spacing with temperature is shown in Fig. 2. The 100 spacing (d_{100}), i.e., the distance between 100 planes, which is strongly fixed by hydrogen bonds and, hence, is less sensitive to temperature variation, shows a slight decrease with increasing temperature. On the other hand, the intersheet distance, $d_{010/110}$, shows a dramatic increase with temperature and equals the value of d_{100} at the transition temperature. Above T_B, the *d* spacing increases slightly owing to normal thermal expansion. No reflections could be observed when the sample was melted.

The nylon 12 12 sample was then rapidly cooled to 175 °C after melting and the course of the isothermal crystallization of nylon 12 12 at 175 °C as followed by X-ray diffraction is shown in Fig. 3a. The crystalline peaks develop slowly with time because the crystallization temperature is rather high (i.e., low supercooling). The single peak at $2\theta = 21.3°$ indicates that nylon 12 12 crystallized into the hexagonal structure during isothermal crystallization at high temperature, which is similar to the behavior of nylon 66 [18] and nylon 46 [17]. Upon further cooling from the crystallization temperature, the sample shows a Brill transition as shown in Fig. 3b. The single peak at high temperature splits into two peaks at about 120 °C on cooling, which is the transformation from the γ phase to the α phase. The changes in spacing of the two characteristic diffraction signals as functions of temperature on cooling are shown in Fig. 4, which shows that the Brill transition of nylon 12 12 is completely reversible but at a little lower transition temperature than the T_B on heating.

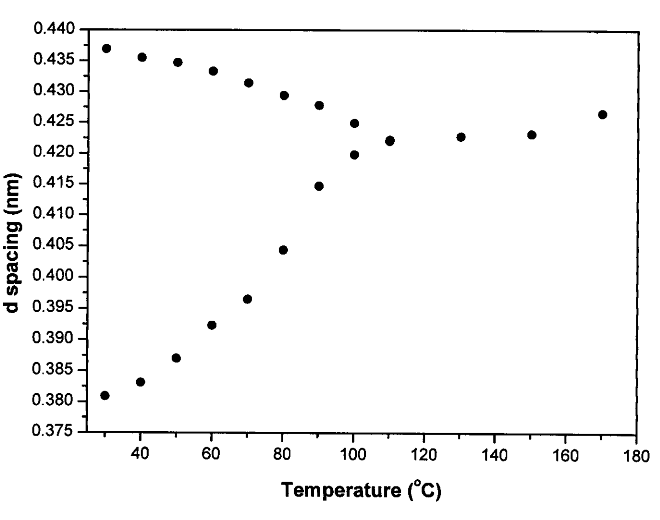

Fig. 2 Plots of the changes in the diffraction spacing as a function of temperature on heating

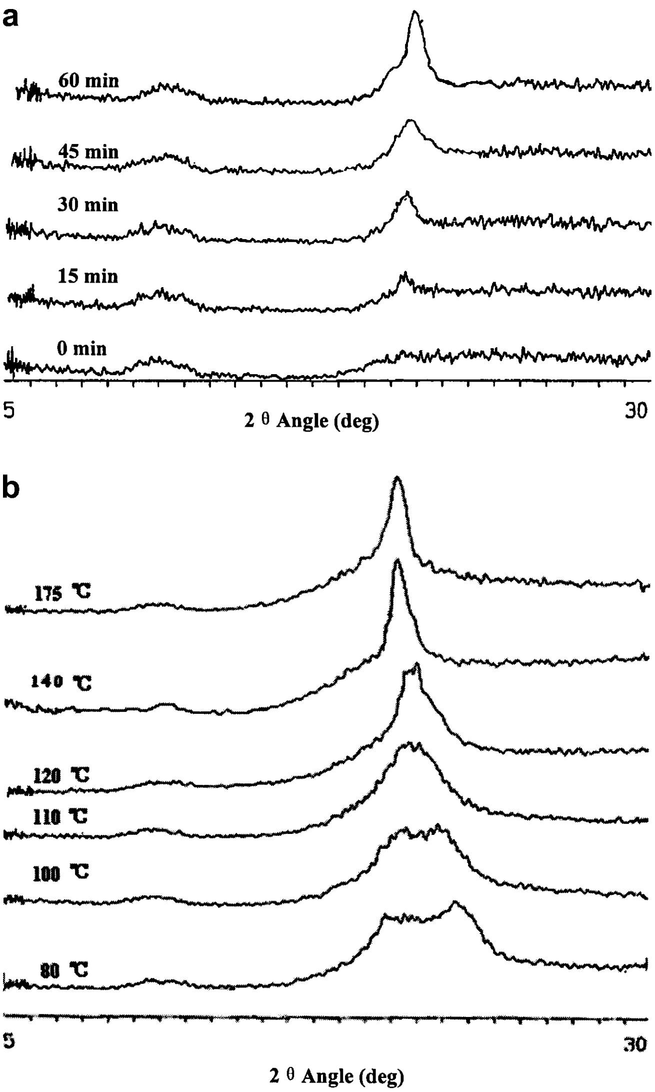

Fig. 3 X-ray diffraction patterns of nylon 12 12 obtained **a** by isothermal crystallization at 175 °C and **b** on cooling from 175 °C to room temperature

In situ FTIR measurements

It has been mentioned that the origin of the Brill transition is the effect of conformational motion of alkane segments; therefore, as an important tool for detecting the conformational structure, fast heating IR spectroscopy is a good technique to display the transformation. Hydrogen bonds play the most important role in determining the crystal structure and the properties of nylons. Are there any changes in the

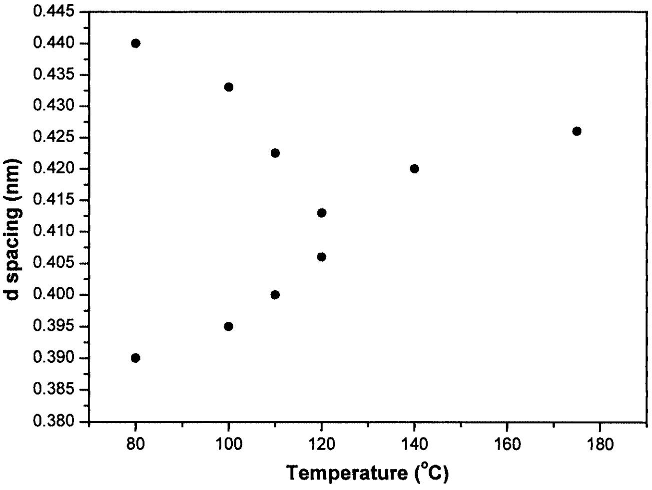

Fig. 4 Plots of the changes in the diffraction spacing as a function of temperature on cooling from 175 °C

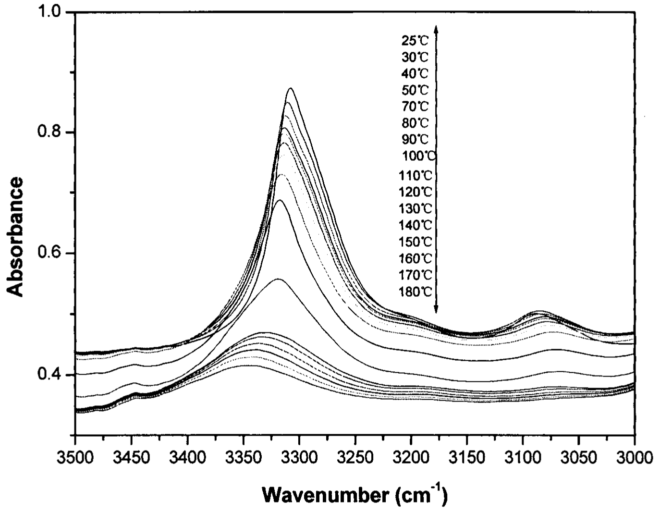

Fig. 5 IR spectra of nylon 12 12 taken as a function of temperature from room temperature to melting in the 3,100–3,500 cm^{-1} region

hydrogen bonds during the Brill transition? Although some studies on the Brill transition measurement with FTIR spectroscopy have been made, there is still no report on the changes in the hydrogen bonds during the Brill transition of nylons. This article reveals a dramatic decrease in the hydrogen-bond strength by the aid of in situ FTIR spectroscopy on heating melt-crystallized nylon samples. For convenience, we describe the results obtained in two major spectral regions separately.

3,100–3,500 cm^{-1} (NH stretching region)

The IR spectra in the range 3100–3500 cm^{-1} for nylon 12 12 recorded as a function of temperature are shown in Fig. 5. On increasing the temperature from 25 to 200 °C, the –NH– stretching band shifts from 3,308 to 3,343 cm^{-1} and there is a steady increase in the breadth of the band. In addition, the total area of the band decreases. The dependencies of the normalized area and the shift of the –NH– stretching bond on temperature for nylon 12 12 are shown in Fig. 6. It can be found that the normalized area decreases dramatically at 110–130 °C and at 190°C, while the –NH– stretching band shifts significantly to high frequency in the two temperature regions.

1,350–800 cm^{-1} (fingerprint region)

IR spectra taken as a function of temperature for nylon 12 12 in the frequency regions 1,100–800 cm and 1,350–1,100 cm^{-1} are shown in Fig. 7a and b, respectively. The band assignment can be carried out by comparison of the spectra obtained for nylon 12 12 with

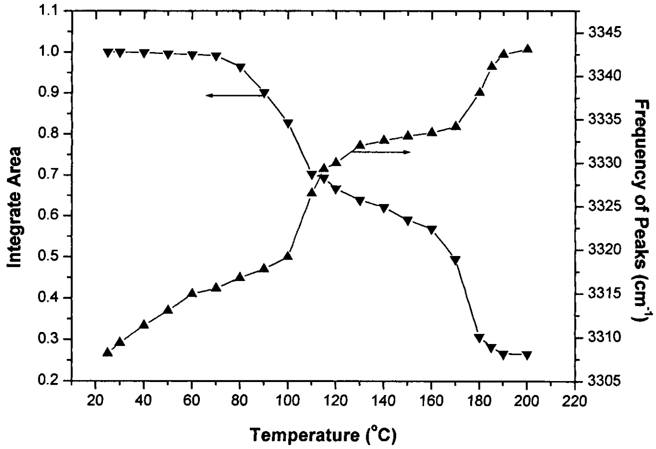

Fig. 6 Temperature dependence of the normalized area and the shift of the –NH– stretching band as a function of temperature

those of nylon 6 and nylon 66 given by Jakes and Krimm [21] and Vasanthan et al. [15]. The band at 943 cm^{-1} is associated with the crystalline phase, while the bands at 1,021 and 1,172 cm^{-1} are associated with the amorphous phase. When we heated a well-crystallized sample from room temperature to the melting temperature (190 °C), the band at 943 cm^{-1} assigned to crystalline bands became weaker and broader, then it disappeared when the sample was melted. In the meantime, the broad amorphous bands (i.e., 1,021 and 1,172 cm^{-1}) remained essentially unchanged with increasing temperature. However, some other bands, at 833, 856, 978, 1,076 and 1,292 cm^{-1}, abruptly disappeared between 110 and 130 °C. We assigned these

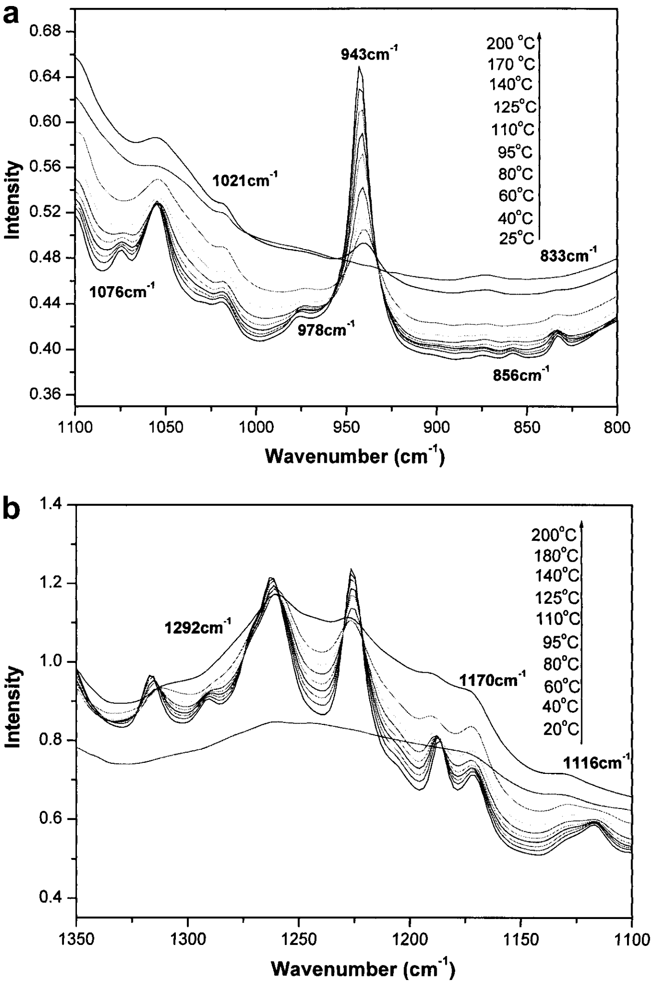

Fig. 7 IR spectra of nylon 12 12 taken as a function of temperature from room temperature to melting in **a** the 1,350–1,100 cm^{-1} region and **b** the 1,100–800 cm^{-1} region

bands to " Brill bands" in accordance with the literature, and they give information on the Brill transition. The integrated absorbency of the vibrational bands at 1,076, 943 and 1,021 cm^{-1}, associated with the Brill band, the crystalline phase and the amorphous phase, respectively, is shown in Fig. 8. The intensities of the Brill bands decrease with increasing temperature and the bands disappear at about 130 °C. The bands of the crystalline phase decrease continuously in intensity and disappear when the sample melts at 190 °C. In contrast, there is almost no change for the amorphous band up to T_m. The changes of these characteristic bands are reversible when cooling from the melting temperature; therefore, the results given by the IR absorption spectra of nylon 12 12 are consistent with the information provided by X-ray diffraction. Nylon 12 12 samples crystallized from melts undergo a Brill transition at about 130 °C.

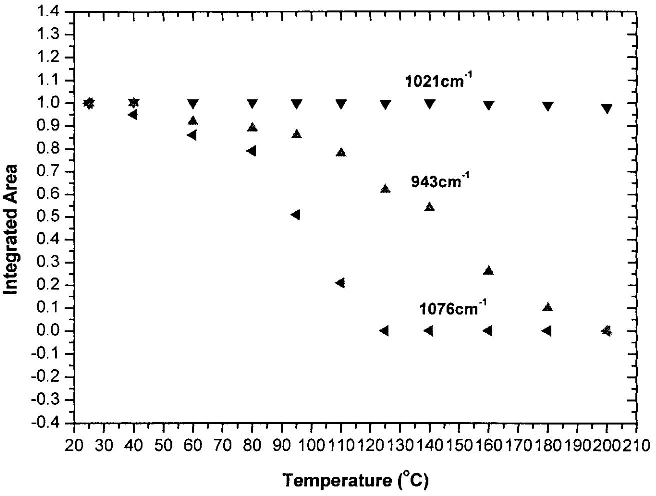

Fig. 8 Temperature dependence of integrated absorbance of the bands associated with the Brill transition, the crystalline phase and the amorphous phase

Discussion

The Brill transition represents a kind of structural change and it occurs while the alkane segments become mobile (local melting); therefore, the Brill transition temperature depends critically on the alkane segment mobility. It is not surprising that the Brill temperature of nylon 12 12 is a little lower than that of nylon 10 10 [22] and nylon 10 12 [23] and much lower compared with that of nylon 6 6 [4]. In addition, the Brill transition temperature of melt-crystallized nylon 12 12 is also much lower than that of the solution-crystallized samples [5]. The difference in the Brill transition temperature probably comes from different crystallization conditions, which result in different crystal perfections.

Extensive research on hydrogen bonds in nylons has been performed using FTIR spectroscopy by numerous researchers [24–30]. It has been found that at room temperature there is essentially 100% hydrogen bonding between –NH– and –CO– in nylons; however, with increasing temperature the total –NH–band area decreases and the –NH– stretching region shifts continuously to high frequency. Early workers [27, 28] made the implicit assumption that the reduction of the total –NH– bands reflects the transformation of some of the hydrogen-bonded –NH– groups into "free" –NH– groups with increasing temperature. However, Skrovanek and coworkers [29, 30] argued that the reduction in the –NH– band area and the shift of the –NH– band are caused by a decrease in the average strength of the hydrogen bonds with increasing temperature and the transformation of hydrogen-bonded –NH– groups to "free" –NH– groups is almost discernable before the melting. In Fig. 6 two dramatic changes in the normalized area and the shift of –NH– stretching bands can be observed at 110–130 and 180–190 °C, respectively. The two regions correspond to the Brill transition and melting of nylon 12 12. The changes may be caused by the dramatic decrease in the hydrogen strength. That is to say, the alkane segment between the amide groups becomes mobile and the conformational motion of the alkane segment reduces the hydrogen bonding strength between the –NH– and –CO– groups in the process of the Brill transition. In other words, although hydrogen bonds remain between the molecular chains during the Brill transition, the hydrogen-bonding strength changes because of the torsion function of the alkane segments. During the melting process of nylon 12 12, the hydrogen-bonding strength also decreases because of the higher mobility of segments and the transformation of some of the hydrogen-bonded –NH– groups into "free" –NH– groups; therefore, the abrupt changes in the total area and the shift of the –NH– bands can be observed in this region.

The 1,350–800 cm^{-1} region is the fingerprint region for nylons, which represents mainly the mobility of the methylene groups; therefore, some bands are found to disappear at the Brill temperature because of the local melting of the alkane segments.

Conclusion

Melt-crystallized nylon 12 12 undergoes a Brill transition at about 130 °C. The transformation temperature is much lower than that of solution-crystallized nylon 12 12 samples reported by Jones et al., and is lower than the crystalline transformation temperatures of nylon 10 10 and nylon 66. When isothermally crystallized, nylon 12 12 at high temperature crystallizes into the pseudohexagonal structure (γ phase) and then transforms into the α phase on cooling. Fast-heating FTIR spectroscopy shows that the hydrogen bonds in nylons change during the Brill transition, i.e., the hydrogen-bond strength decreases dramatically because of the mobility of the methylene groups. In addition, some bands in the fingerprint region can also give apparent information on the Brill transition and several "Brill bands" of nylon 12 12 were also identified.

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