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RESEARCH ARTICLE

XIAO Dan, CUI Xiaowen, LI Weihua, YAN Deyue

Investigation on the Brill transition of polyamide 618

Abstract The Brill transition of even–even polyamide 618 was investigated using differential scanning calorimetry (DSC), temperature-dependent wide angle X-ray diffraction (WAXD) and Fourier transform infrared (FTIR). The X-ray diffraction results indicate that the melt-crystallized sample of polyamide 618 transforms from the triclinic unit cell to the pseudo-hexagonal phase in the range of 120–180°C. In this range, the thermograph of polyamide 618 presents a broad endothermal peak. From the FTIR spectra, it was found that during the transition process of polyamide 618, the intensity of the intra-sheet hydrogen bonds becomes weak. At the same time, the CH_2–amide bonds twist, and the all-*trans* conformation of methylene sequences is disordered by inserting the gauche conformation. The CH_2 segments are in a mobile state because of the enhanced stretching and twisting vibrations of the C–CO and C–N bonds.

Keywords Brill transition, polyamide 618, conformation, triclinic, pseudo-hexagonal

1 Introduction

Most of aliphatic polyamides show a crystal-to-crystal transition when heating from room temperature to their melting points. This phenomenon is named as the Brill transition and easy to be observed using wide angle X-ray diffraction (WAXD) [1–4]. In WAXD profiles even–even nylons present two strong diffractions at *d*-spacings of 0.44 nm and 0.37 nm (100 and 010/110 diffractions) at room temperature, indicating a typical triclinic lattice (α-form). In a heating process the two diffractions approach gradually and merge into a single diffraction peak at a *d*-spacing of 0.42 nm before melting, which represents the characteristic pseudo-hexagonal unit cell [5–7]. Besides variable-temperature WAXD, some other techniques have also been adopted to detect the Brill transition, such as real-time Fourier transform infrared spectroscopy (FTIR) [8], small angle X-ray scattering (SAXS) [9], differential scanning calorimetry (DSC) [10] and nuclear magnetic resonance (NMR) [5].

In the triclinic lattice of even–even nylons at room temperature, the molecular chains form intra-sheet hydrogen bonds and the hydrogen-bonded sheets stack together in a progressive mode or an alternative mode via Van der Waals force. The molecular chains adopt the *trans*-zigzag conformation [7]. Fig. 1 shows the schematic diagram of triclinic crystal structure of polyamide 618 projected parallel to the chain axis. Above Brill temperatures of even–even nylons (the lowest temperature at which the projected inter-chain distance within hydrogen-bonded sheet equals to the inter-sheet spacing), the triclinic phase is replaced by the pseudo-hexagonal crystalline structure [11]. However, in the pseudo-hexagonal phase, how do the molecular chains constitute the unit cell, especially what are the arrangement of hydrogen bonds and the state of methylene sequences? Several assumptions have been put forward to explain this crystalline transition. Some researchers suggest it is the anisotropy of thermal expansion of the nylon crystal lattice in different directions that leads to this phenomenon [12]. Other works point out that the Brill transition originates from the 'local melting' of the methylene sequences while the integrity of H-bonded sheets keeps intact [4,5,13]. It has been also reported that the transition is related with the transformation from two-dimensional H-bonded sheets to three-dimensional H-bonded network [14,15]. Although so many research works were carried out to clarify the essential feature of this Brill transition, there are still some unclear parts of the concrete structural change about the methylene segments and amide groups.

The vibrational spectroscopy, for example FTIR, is a useful method for giving us much important information about the change of the molecular chains during the crystalline transition [4,8]. Vasanthan et al. investigated the Brill transition behavior of nylons 66 and 6 by infrared spectroscopy [8]. He found that some IR bands disappeared at Brill temperature (abbreviated as T_B) and termed them as 'Brill bands', their changes were associated with the 'local melting' of methylene segments. However, the details of the

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XIAO Dan, CUI Xiaowen, LI Weihua, YAN Deyue (✉)
College of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China
E-mail: dyyan@sjtu.edu.cn

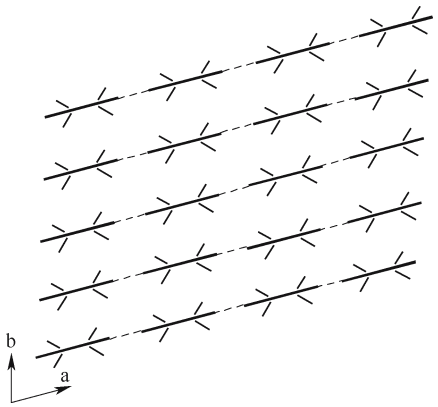

Fig. 1 Scheme of triclinic crystal structure of polyamide 618 projected parallel to the chain axis. The hydrogen bonds are indicated by dashed lines

crystalline transition are unclear. Recently, some papers were published to present the conformational change of the methylene moiety during Brill transition of even-even polyamides [16,17].

Nylon 618 includes long methylene sequences between the diacid moieties which are helpful for detecting the motion of the long methylene units during the Brill transition process [18]. By measuring the changes of the vibration of amide groups and the conformation changes of the methylene sequences, it is helpful for us to understand the mechanism in the crystalline transition of even-even nylons.

2 Experimental

2.1 Sample preparation

Polyamide 618 was synthesized from 1,6-diaminohexane and 1,16-octadecanedioic acid [18]. The melt-crystallized sample was prepared by pressing polyamide 618 at 220°C and air cooled to room temperature. The thickness of the sample for WAXD is 1 mm and that for FTIR is about 20 μm.

2.2 Differential scanning calorimetry (DSC)

Melting temperature of the polyamide sample was measured on a Perkin-Elmer Pyris-1 series (Q10 V3.7 Build 249) differential scanning calorimeter at a heating rate of 10°C/min. A nitrogen purge was provided throughout the DSC scan.

2.3 Variable-temperature WAXD

WAXD experiments were carried out on a Rigaku Dmax-rc X-ray diffractometer equipped with a high temperature sample-chamber at 40 kV and 100 mA. Ni-filtered CuKα radiation was used. The heating rate was 5°C/min, and the sample was held for 2 minutes at each measuring temperature before collecting data.

2.4 Real-time FTIR spectroscopy

IR spectra were studied on a Bruker Equinox-55 Fourier transform infrared spectrometer equipped with a variable-temperature cell at a resolution of 2 cm^{-1}. The sample was heated at a rate of 5°C/min. At the same time, FTIR spectra were collected at an interval of one minute. Sets of 8 scans were used for signal average.

3 Results and discussion

3.1 DSC Thermograms

In the DSC thermogram of the melt-crystallized sample of polyamide 618 (see Fig. 2), it is obvious that its melting temperature (T_m) is 201°C. In the range of 120–190°C, a broad endothermal peak was found, where the thermal motion was considered to occur as will be discussed later. From the DSC results it is speculated that the crystalline transition occurs in this range just below the melting temperature. The similar results were observed in the DSC scan of nylon 66 [19]. The structural change of polyamide 618 will be discussed in the following part.

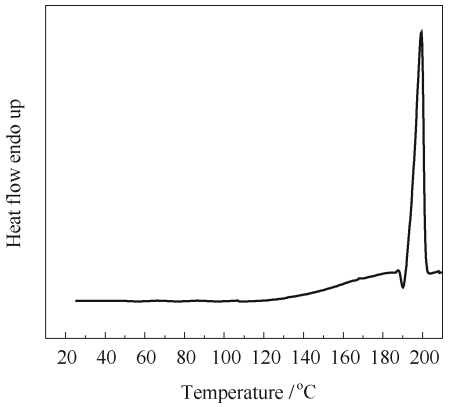

Fig. 2 DSC thermograms of a melt-crystallized sample of polyamide 618

3.2 Temperature-dependence of WAXD

Figure 3 shows the temperature-dependence of the diffraction spacings of the melt-crystallized sample. It was found that the inter-sheet distances increase more quickly than the declining of the inter-chain distances within the H-bonded sheets during the heating process, because the inter-sheet interaction is weaker than the force fixing the chains together within the hydrogen-bonded sheets [20–23]. Thus, it can be understood that the Van der Waals interaction between the inter sheets decreases remarkably as temperature increases. From Fig. 3 it can be seen that the Brill transition of the melt-crystallized sample of polyamide 618 is completed at 180°C. In addition, the changes of diffraction spacings are

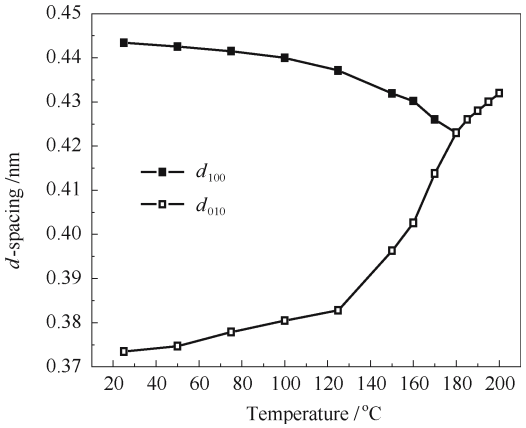

Fig. 3 The diffraction spacings as a function of temperature in the heating process for polyamide 618

remarkable in the range of 120–180°C, which coincides with the data of the DSC analysis.

3.3 Temperature-dependence of FTIR

3.3.1 Changes in the amide group bands

Figure 4 (a–e) present the FTIR spectra of the melt-crystallized sample under study as a variable of temperature in the ranges of 3000–3500 cm^{-1}, 1300–1500 cm^{-1}, 1100–1300 cm^{-1}, 750–1150 cm^{-1} and 500–800 cm^{-1}, respectively. At room temperature, polyamide 618 shows the infrared spectrum with characteristic bands of the triclinic structure at around 580 cm^{-1} and 540 cm^{-1} (amide VI, C=O out-of-plane bending), 680 cm^{-1} (amide V, NH-out-of plane bending) and 3300 cm^{-1} (amide A, hydrogen-bonded N–H stretching). In addition, the strong absorbance bands at about 3090 cm^{-1} (amide B, overtone of amide II), 1640 cm^{-1} (amide I, C=O stretching), 1540 cm^{-1} (amide II, C−N stretching) and 940 cm^{-1} (amide IV, C−CO stretching). Moreover, the typical bands at around 1370 cm^{-1}, 1285 cm^{-1}, 1247 cm^{-1}, and 1215 cm^{-1} belong to amide III coupled with the out-of-plane vibration of methylene units [4,8,17,18,24].

On heating up the sample, these amide group bands become weaker in intensity and broader in profile. At the same time, their peak positions shift up or down. Figure 5 presents the plots of integrated absorbance and peak position of amide A as a function of temperature. From this figure it is seen that the peak position of amide A band moves to higher wave numbers slightly below 120°C and shifts dramatically to the high wave-number side in the range of 120–180°C as temperature increases. At the same time, the integrated absorbance of amide A decreases gradually below 120°C and reduces remarkably beyond 120°C when heating. The peak wave-number of amide A band is related directly with the strength of the inter-chain hydrogen bonds [25,26]. The up-shift of amide A band with temperature originates from the weakening of hydrogen bond intensity. From Fig. 4(a), it can be found that a weak peak at around 3452 cm^{-1} appears at 120°C and rises as temperature increases. This peak is associated with the free NH groups in the polyamide sample under consideration. Therefore, it can conclude that the hydrogen bonds become weaker gradually and dissolve partly into the free NH groups in the crystalline transition region.

Figure 4(e) shows the infrared spectra in the range of 500–800 cm^{-1} at various temperatures. Amide VI band moves also to the higher frequency side with temperature increased while the amide V band almost retains in the same position. These two bands are also affected by the hydrogen bond strength. Because the two bands originate from the out-of-plane vibration of NH and CO groups, it is considered that the shifts of amide V and amide VI are sensitive to the twisting motion of the CH_2–NH and CO–CH_2 bonds, respectively [24]. The slight band shifts and broadening of amide VI may be the result of the twisting motion around the CH_2–amide bonds as well as the variation of hydrogen bonds.

A similar but more remarkable change is found for the amide IV band at 940 cm^{-1} characteristic of C–CO bond stretching vibration mode (ν[C–CO]) [17]. The homologous movement is detected for stretching vibration mode of C–NH bond (ν[C–NH]) at 1184 cm^{-1}. Figure 6 shows the integrated absorbance and half-width of amide IV band taken as a function of temperature. Like amide A, the integrated absorbance of the band at 940 cm^{-1} almost does not change below 120°C and declines evidently in the region of 120–200°C as temperature increases. At the same time, this band becomes broader gradually and the half-width of the band rises obviously. The half-width of the band strongly depends on the activity of the thermal motion of the corresponding chemical group. The remarkable increasing observed in half-width of ν[C–CO] band indicates the enhancement of twisting motion of the CH_2–CO bond. The analogous trend is considered to occur for the ν[C–NH] band at 1184 cm^{-1}.

In addition, it needs to be mentioned that it is difficult to explain the change of amide III bands at around 1370 cm^{-1}, 1280 cm^{-1}, and 1240 cm^{-1} on the heating process because of the complicated interaction between the amide groups and the methylene units [24,27]. The amide B peak weakens and broadens on heating, however, amide I and II peaks maintain nearly unchanged during all the continuous heating process.

Two other bands are seen at around 1420 and 1470 cm^{-1} which belong to the scissoring vibration of CH_2 units next to CO and NH groups, respectively [24,27]. On heating, these two bands decline in intensities and broaden their profiles gradually. At the same time, the 1420 cm^{-1} band shifts to a higher wave-number side while the 1470 cm^{-1} band moves to the lower frequency. All the changes are the result of the strengthening of the vibration motion and the twisting motion of the CH_2–amide bonds.

From changes of all the amide group bands, it can be confirmed that the twisting motion of the amide–CH_2 bonds enhances and the strength of hydrogen bonds becomes weak. These variations are accelerated in the crystalline transition region of polyamide 618.

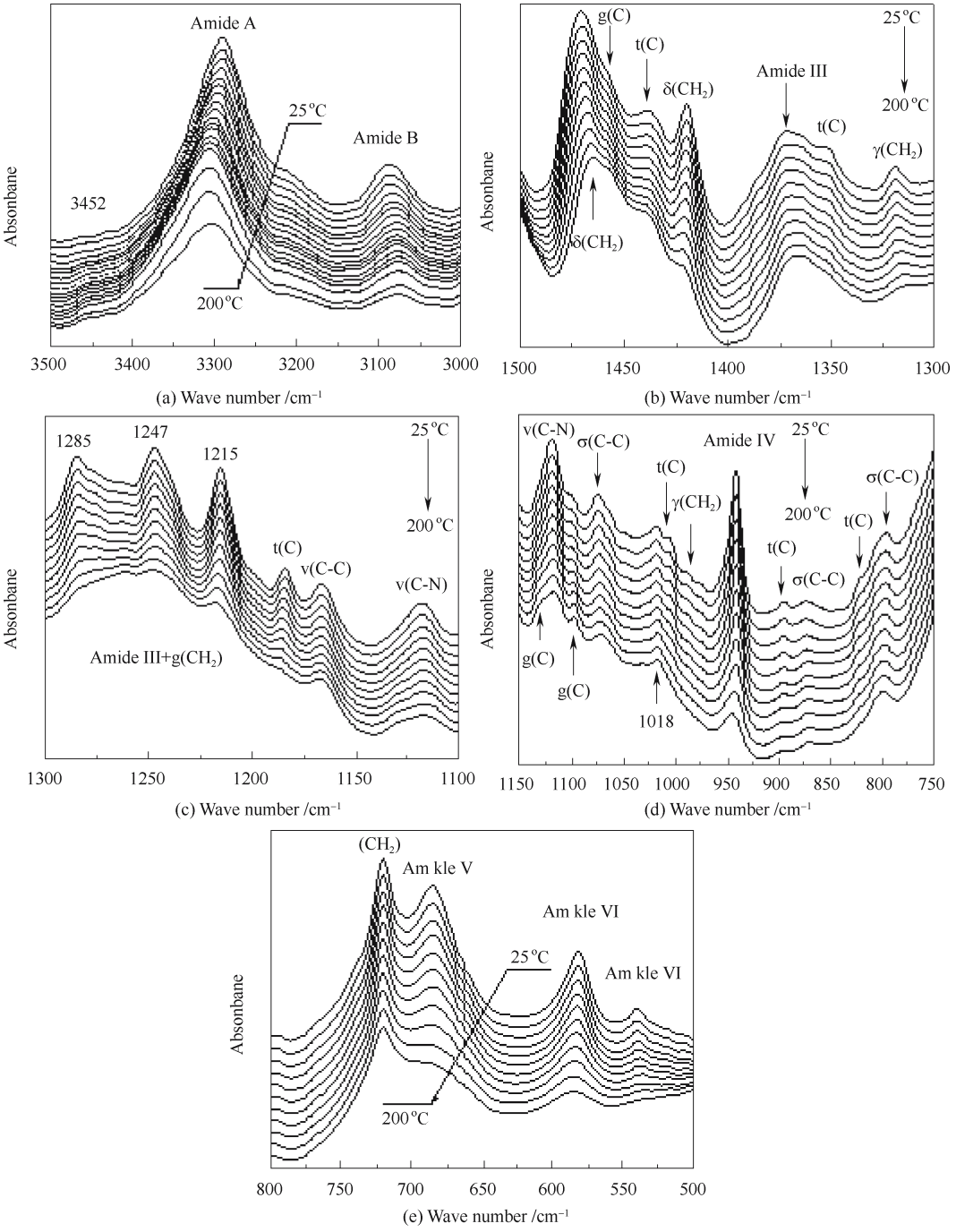

Fig. 4 Infrared spectra of polyamide 618 taken at various temperatures. Spectra in the frequency regions of 3000–3500 cm^{-1} (a); 1300–1500 cm^{-1} (b); 1100–1300 cm^{-1} (c); 750–1150 cm^{-1} (d); 500–800 cm^{-1} (e)

3.3.2 Conformation of methylene segments between the hydrogen-bonded amide groups

Polyamide 618 has a long methylene sequence between the diacid segments. At room temperature, the methylene units adopt a planar-zigzag conformation. Infrared spectra give some important information on the conformation of methylene segments. In Fig. 4(e), the band at 721 cm^{-1} is assigned to the most-in-phase methylene rocking vibration mode [$\nu(CH_2)$] which is a characteristic of the triclinic packing structure of *n*-alkane [28–30]. Therefore, the subcell of methylene sequences of nylon 618 is considered to adopt the triclinic structure, which is coincident with the X-ray diffraction data presented in the previous section. When the sample is heated, the intensity of the 721 cm^{-1} band declines, and the band is seen to shift gradually toward the pattern intrinsic of the hexagonal stacking structure of the methylene chains, but it is not very clear because of the broad spectral band

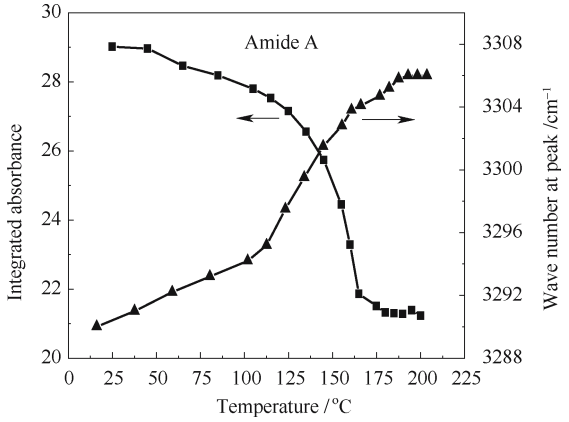

Fig. 5 The integrated absorbance and peak position of amide A band as a function of temperature, respectively

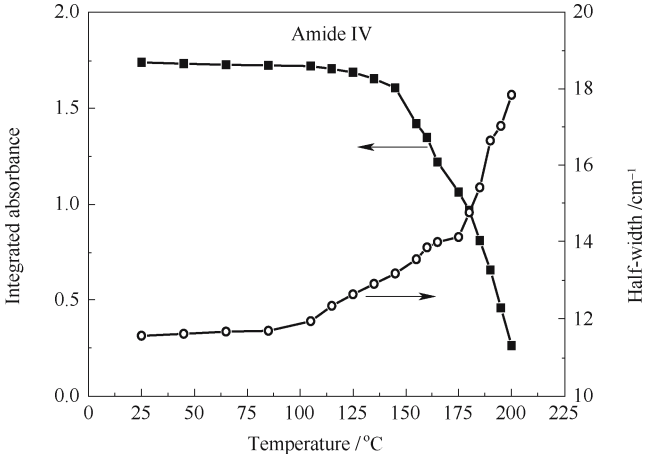

Fig. 6 The temperature-dependence of the integrated absorbance and half-width of amide IV, respectively

[17,29,30]. At the same time, the CH_2 scissoring band (for all the methylenes not adjacent to the amide group) is observed at around 1438 cm^{-1} at room temperature, the profile of which reflected the triclinic stacking structure of the mehtylene zigzag parts. With temperature increased, the band decreases its intensity and broadens its profile, suggesting the transformation from the triclinic packing of methylene parts to the pseudo-hexagonal stacking and the existence of conformationally disordered methylene sequences. The similar change of methylene band is observed at around 1318 cm^{-1} which is assigned to the CH_2 bending vibration. These spectral variations indicate that the triclinic crystalline structure of methylene sequences converts gradually to the pseudo-hexagonal packing mode in the higher temperature region.

On the other hand, comparing to the vibration bands of methylene segment, the pure conformational bands are very weak and difficult to be measured precisely. Here, two weak shoulder bands at around 1350 and 1457 cm^{-1}, which belong to the *trans* conformation and the gauche conformation of the methylene part, respectively, are selected to follow their changes during the heating process. Figure 7 shows the integrated absorbance of the two bands as a variable of temperature. From this, the trend can be seen that the intensity of the band at 1350 cm^{-1} decreases with the increasing temperatures while that of the band at 1457 cm^{-1} goes up, indicating that the decreasing of the *trans* conformation and the increasing of the gauche conformation in the methylene segments. The *trans*-zigzag conformation of the methylene sequences in the triclinic crystalline structure at room temperature becomes disordered by inserting of the gauche conformation of methylene units which exist in the pseudo-hexagonal crystalline structure of the even-even nylon under study at high temperature. Other conformation bands were also observed at 1350, 1184, 1130, 1096, 1004, 894, and 822 cm^{-1}. However, it is difficult to estimate the content of the methylene units with the gauche conformation until now. Therefore, in the methylene part of the pseudo-hexagonal phase at high temperature region, the *trans*-zigzag conformation and the gauche conformation coexist at the same time. The molecular chains become disordered and mobile.

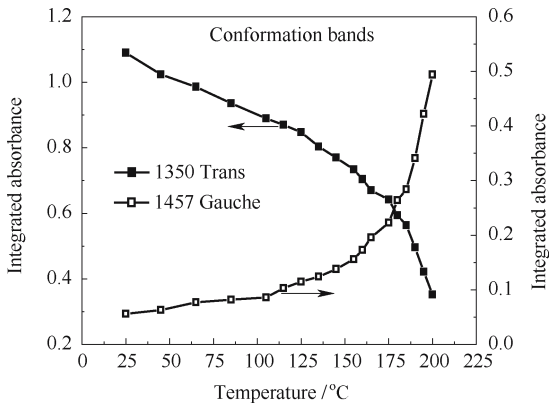

Fig. 7 The plots of integrated absorbance of the all-*trans* and gauche conformation bands of methylene units between the amide groups, respectively

3.4 The crystalline transition of polyamide 618

X-ray diffraction data give the information that the prominent *d*-spacings of the nylon crystal change upon heating. In the region of 120–180°C, these changes enhance, suggesting that the crystalline transition takes place in this temperature range. As already discussed, the infrared spectral variations were analyzed to know about the variation of the three kinds of groups including amide groups, methylene units, and CH_2–amide bonds.

In a heating process the amide A band shifts to high frequency side and broadens gradually. At the same time the amide A, amide V and amide VI bands become weaker and weaker in intensity, indicating that the strength of hydrogen bonds declines with increasing temperature. The band at 940 cm^{-1} is related with the CH_2–amide bonds and its half-width reflects the twisting motion of the CH_2–amide bonds. In our results, the weakening of the intensity of the hydrogen bonds is accepted. Meanwhile, the enhanced twisting motion of CH_2–amide bonds also weakens the hydrogen bonds.

According to the changes of the bands at around 1350 and 1457 cm^{-1} with increasing temperature, the conformation of methylene sequences transforms distinctly from the *trans*-zigzag conformation at room temperature to the gauche conformation at high temperature. It is consistent with the results of the change of Brill bands that was discussed in the preceding section. The CH_2 unit bands at 721, 1318 and 1438 cm^{-1} decrease in intensities and broaden gradually on heating, illustrating that the triclinic crystalline structure transforms gradually to the pseuso-hexagonal subcell. The enhanced vibration and twisting motion of CH_2 units make them in the mobile state, and the ordered *trans*-zigzag conformation of methylene sequences becomes a mixture of disordered *trans* and gauche conformation of CH_2 units in the crystalline transition process.

4 Conclusions

In this work, the Brill transition of nylon 618 was investigated by variable-temperature WAXD and FTIR spectroscopy. The essential characteristics can be summarized as follows based on the results discussed in this article:

(1) The Brill transition of nylon 618 is a continuous process in a temperature range of 120–180°C and can be divided into two stages according to the variations of the typical diffraction spacings in WXAD patterns and the characteristic absorbance bands in FTIR spectra during the heating process. The first stage is below 150°C, and the last stage is above it.

(2) In the first stage, the anisotropy of thermal expansion in different directions in the crystal lattice of nylon 618 is the prominent reason for the changes of the diffraction spacings. The crystal retains a triclinic structure, and the hydrogen bonds become weak due to the thermal motion of the molecular chains. There are no inter-sheet hydrogen bonds and twisting in the CH_2–amide bonds. The molecular chains almost maintain the *trans* conformation.

(3) In the last stage, the intensity of the hydrogen bonds becomes continuously weak with increasing temperature. The twist of the CH_2–amide bonds enhances, including the C–CO and the C–N bonds. Thus, the in-plane hydrogen bonds tilt and the *trans*-zigzag conformation of the molecular chains is distorted. The gauche conformation in the methylene sequences increases. The stretching, scissoring, and wagging vibrations of methylene units are strengthened and the methylene segments between the amide groups are in a mobile state.

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