Polymer Bulletin 49, 387–394 (2003)

Polymer Bulletin

Different Crystalline Transition Behavior in Polyamides 12 16, 10 16 and 8 16

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Summary

Crystalline transition behavior of polyamides 12 16, 10 16 and 8 16 was studied systematically by variable-temperature WAXD and real-time FTIR. It is surprising that the crystalline transition behavior of these polyamides is different from one another. Brill transition was observed before melting on heating for nylon 8 16 in both single crystal and melt-crystallized samples. For nylon 12 16, Brill transition of the sedimented crystal mats did not occur below its melting point, while the melt-crystallized sample showed the crystalline transition before melting on heating. Furthermore, the Brill temperature could not be detected in both single crystal and melt-crystallized samples of nylon 10 16. A further investigation on the FTIR spectra of –NH– groups upon heating presented helpful information for understanding the mechanism of the crystalline transition.

Introduction

Polyamide, generally known as nylon, represents a significant family of semi-crystalline polymers and is widely used in many fields due to its unique comprehensive properties. The characteristic crystal structure in nylons originates from the formation of hydrogen bonds between amide groups.

Even-even nylons form lamellar crystals at room temperature, which are composed of chain-folded hydrogen-bonded sheets. The requirement that all hydrogen bonds between adjacent chains should be linear (or close to linear) dominates the crystal structure of nylons. There are two ways in stacking of these chain-folded hydrogen-bonded sheets, namely α phase for progressive staggering and β phase for alternating staggering. Both of them show two characteristic peaks at spacing of 0.44nm and 0.37nm in X-ray diffractogram, which correspond to the inter-chain distance within hydrogen-bonded sheet and the inter-sheet spacing respectively. Pseudo-hexagonal structure is another pattern observed in even-even nylons, which is usually found at high temperature and gives a single reflection at spacing of 0.42nm in X-ray diffractogram.

Most even-even nylons withヲ orヲ structure undergo a crystal-to-crystal transition upon heating known as Brill transition [1-4]. Brill temperature (T_B) represents the lowest temperature at which the projected inter-chain distance within hydrogen-bonded sheet equals the inter-sheet spacing. Brill transition is easily observed in variable-temperature Wide-angle X-ray Diffraction (WAXD). Upon heating, the two strong characteristic diffraction signals at 0.44nm and 0.37nm approach each other, and merge into a single reflection at spacing of 0.42nm. The mechanism of the transition is still in discussing [5-8]. Additionally, real-time Fourier Transform Infrared (FTIR) has also been adopted to follow Brill transition in nylon 6, nylon 6 6 [9] and nylon 10 12 [10].

It is known that the melting temperature (T_M) of even-even nylons increases with the density of linear hydrogen bond. There is a similar trend in crystalline transition temperatures of even-even nylons reported previously. A comparison between T_M and T_B of various even-even nylons has been demonstrated by Atkins [2, 11, 12]. The authors attributed the result of T_B equal to T_M for some nylons either to the low melting points or to the high Brill temperatures [2]. In fact, there is no one fixed Brill temperature for a particular nylon. The measured T_B is dependent on crystallization conditions and varies with the perfection of the crystals [12]. It has been reported that melt-crystallized nylon 6 6 [13] and lamellar crystals of nylon 8 [14] show obvious variations in T_Bs with the crystallization conditions. In this paper, Brill transition of three even-even nylons with long alkane segments, including nylons 12 16, 10 16 and 8 16, has been investigated by variable-temperature WAXD and real-time FTIR, and their crystalline transition behavior observed is different from each other. The effect of crystal preparation conditions on Brill temperatures of these polyamides has been studied and the mechanism of Brill transition has been discussed.

Experimental

Sample preparation

Polyamides 12 16, 10 16 and 8 16 were synthesized by the common melt polycondenstation based on 1,14-hexadecane diacid and various diamines. The molecular weights of the resulting polymers are between 1.5×10^4 and 2.0×10^4 determined by intrinsic viscosity in dichloroacetic acid at 25。 0.1°C. The details of the syntheses were described elsewhere [15]. The films with the thickness of 20_m for IR measurements were obtained by hot pressing beyond melting point, followed by annealing at 130°C for 6 hours. Thick films of melt-crystallized samples for WAXD experiments were processed with the similar method. Single crystals of polyamides under consideration were grown at the temperature around 130°C after resolving. Sedimented mats of single crystals were prepared using the following procedure as mentioned in the references [8, 11, 16]. The crystal suspensions of these polymers were grown from the solutions in 1,4-butanediol (0.2% w/v) and hot-filtered, followed by annealing in a vacuum oven at 100°C for 24 hours.

Variable-temperature WAXD

Variable-temperature WAXD measurements were performed on a Ragaku Dmax-rc X-ray diffractometer with Cu Kヲ ヂ radiation (40KV, 100mA) equipped with a high temperature specimen-chamber. After having been placed into a platinum holder, the sample was heated to the desired temperature at a rate of 5°C/min and held at this temperature for 2 minutes before commencing the data collection.

Real-time FTIR spectroscopy

Infrared spectra were recorded using a Bruker Equinox-55 FTIR spectrometer fitted with a variable temperature cell. The sample was heated at a rate of 5°C/min and the IR spectra were collected every minute.

Differential Scanning Calorimetry (DSC)

The melting temperatures of sedimented mats of the nylons investigated were measured using a Perkin-Elmer Pyris-1 differential scanning calorimeter under nitrogen purge at a heating rate of 10°C/min.

Results and Discussion

Different crystalline transition behavior in polyamides 12 16, 10 16 and 8 16

Both melt-crystallized sample and sedimented mats of the nylons under consideration have been measured by variable-temperature WAXD. When the melt-crystallized nylon 12 16 is heated, the two reflections approach each other gradually and merge into one before melting (Figure 1(a)). It suggests that Brill transition occur in this sample at about 160°C. Moreover, Figure 1(b) gives the WAXD patterns of sedimented crystals mats of nylon 12 16 upon heating. It is seen that the two diffractional peaks do not merge before melting although they move together with increasing temperature.

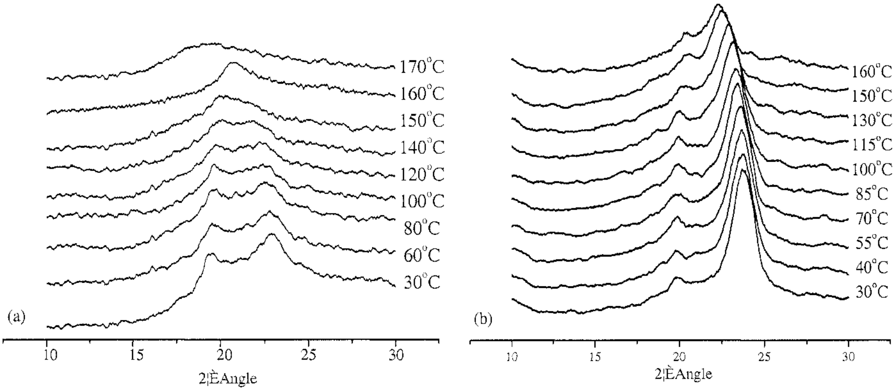

Figure 1. WAXD patterns of polyamide 12 16 in a continuous heating process: (a) melt-crystallized sample; (b) sedimented mats of single crystals.

A further study on d-spacing variation with temperature implies that the T_B of single crystals of nylon 12 16 is higher than its T_M (Figure 2). This phenomenon has been observed in nylon 10 12 [8], which is somewhat different from the results reported by

Atkins [2, 11, 16]. Atkins revealed that some nylons have extrapolated T_Bs coincident with their T_Ms. Since the melting temperature of nylon 12 16 is rather low (170°C, measured by DSC), the single crystals of nylon 12 16 has an extrapolated T_B higher than T_M. It has been reported that T_B varies with the perfection of the crystals and there is no fixed Brill temperature for a particular nylon [12]. Melt-crystallized sample and single crystals display the two extremities of the crystalline perfection. Hence the difference in Brill temperatures for the two samples results from the different crystalline perfection related to the preparation conditions.

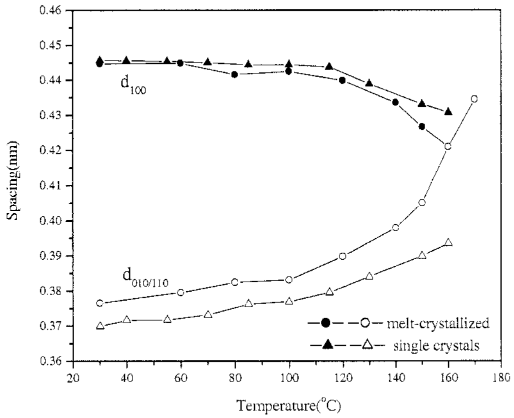

Figure 2. Plots of variation in d-spacing of polyamide 12 16 with temperature

Interestingly, Brill transition does not occur in polyamide 10 16 before melting on heating for both melt-crystallized sample and single crystals. The two diffraction peaks in WAXD traces do not meet with each other upon heating even though they become closer and closer. It is seen that the extrapolated T_B and T_M for melt-crystallized nylon 10 16 are coincident, while the single crystals have T_B higher than its T_M. It is not surprising to find that the T_B of sedimented mats of nylon 10 16 is higher than T_M since the melting temperature of nylon 10 16 is as low as 176°C (measured by DSC). Nevertheless, the fact that the melt-crystallized nylon 10 16 has the T_B equal to T_M is beyond our anticipation, because the crystalline perfection of melt-crystallized sample is usually poor. To our knowledge, nylon 10 16 is the only one of nylons that no Brill transition can be observed below the melting temperature even for the melt-crystallized sample. Figure 3 gives the d-spacing changes of nylon 10 16 with increasing temperature.

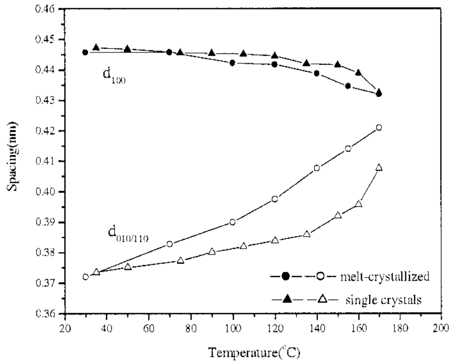

Figure 3. Variation of d-spacing with temperature for polyamide 10 16

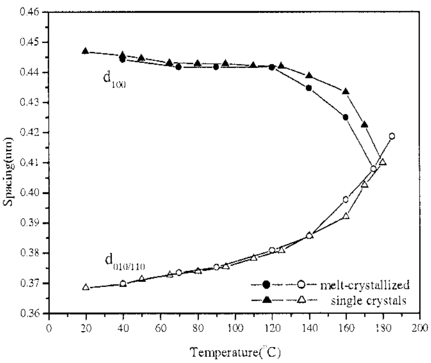

Figure 4. Variation of d-spacing of polyamide 8 16 during heating process

Brill transition behavior in polyamide 8 16 samples reveals another style, which is different from those of polyamides 12 16 and 10 16 (see Figure 4). Both melt-crystallized and single crystal samples of nylon 8 16 show their crystalline transition before melting on heating, while the T_B of sedimented mats (180°C) is higher than that of the melt-crystallized sample (175°C). The melting temperature of nylon 8 16 is 189°C measured by DSC, which is high enough to allow the occurrence of Brill transition of the single crystals before melting. The difference between two T_Bs of the single crystals and melt-crystallized samples also comes from the variation of the crystalline perfection.

T_B and T_M of all nylons under consideration are collated in Table 1. The phenomenon that the crystalline transition behavior of polyamides 12 16, 10 16 and 8 16 is different from one another deserves a further discussion. It has been pointed out that T_B is more closely related to the detailed interchain hydrogen bond arrangement rather than the average amide density because Brill transition is the consequence of the rearrangement of hydrogen bonds within the crystal [8]. Consequently, the match of alkane segment length between amine groups with that between acid groups may influence the arrangement of hydrogen bonds, which leads to the different crystalline transition behavior of the nylons studied in this work.

Table 1 Melting temperatures and Brill temperatures for polyamides 12 16, 10 16 and 8 16 (°C)

	Nylon 12 16	Nylon 10 16	Nylon 8 16
T_M	170	176	189
T_B (single crystals)	—	—	180
T_B (melt-crystallized)	160	176 (extrapolated)	175

Real-time FTIR studies and discussion on mechanism of Brill transition

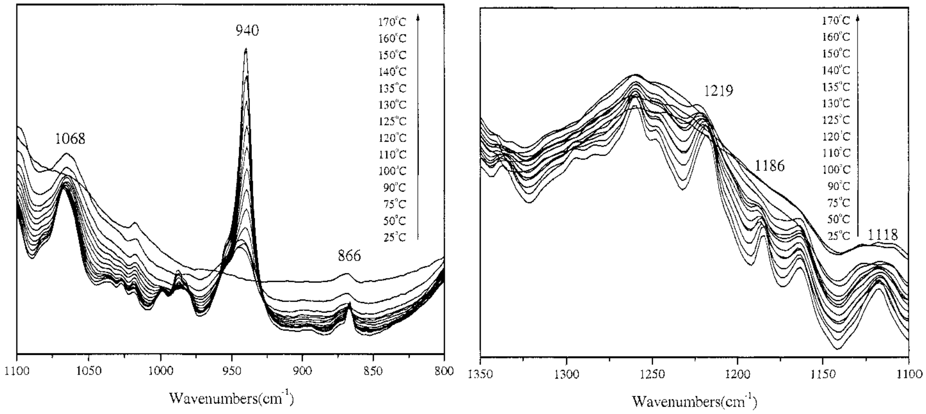

Figure 5. Infrared spectra of polyamide 12 16 taken from room temperature to melting

Figure 5 shows real-time FTIR spectra of the melt-crystallized sample of polyamide 12 16. The frequency ranges of 1350-1100cm^{-1} and 1100-550cm^{-1} have been selected since several typical absorption bands locate at these regions. For instance, the band at

866cm^{-1} and 1118cm^{-1} are associated with amorphous phase, whereas the band at 1219cm^{-1} and 940cm^{-1} are correlated with crystalline phase. When the sample is heated from room temperature to its melting point, those crystalline bands become weaker and broader. However, the bands assigned to amorphous phase almost remain during the heating process. In addition, some other bands disappear abruptly around 150°C, such as the bands at 982cm^{-1}, 1068cm^{-1}, 1164cm^{-1}, 1186cm^{-1} and 1260cm^{-1}. The band at 1068cm^{-1} is due to the skeletal C-C stretch vibration and the band at 982cm^{-1} reflects the –NH– rocking mode [9]. The temperature at which these bands disappear (i.e., 150°C) is consistent with the T_B of melt-crystallized nylon 1216 determined by WAXD (160°C) regarding the deviation of different measurements. Therefore, these bands can be identified as "Brill bands" for nylon 12 16.

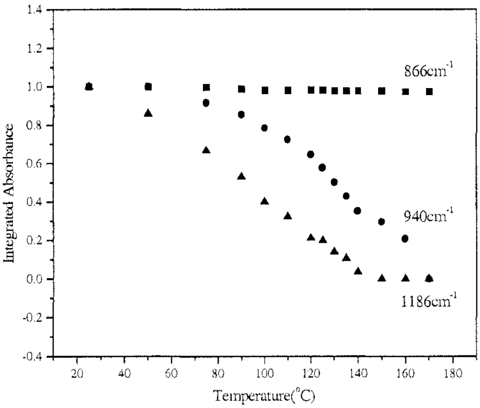

Figure 6. Temperature dependence of the integrated absorbance of the different types of bands for polyamide 12 16

Figure 6 shows the integrated absorbance of infrared bands associated with the three types of phases. It can be seen that the Brill band decreases with increasing temperature and disappears at T_B, while the crystalline band declines continuously and disappears in the melt. On the contrary, the amorphous band shows little change up to T_m.

A further investigation on the frequency range of 3500-3000cm^{-1} of nylon 12 16 will help us to understand the mechanism of Brill transition since the peak at 3317cm^{-1} originates from the stretch vibration of –NH– groups. As shown in Figure 7, the absorption intensity at 3317cm^{-1} lessens and the peak broadens upon heating. In the mean time, the peak value moves to a higher wave number.

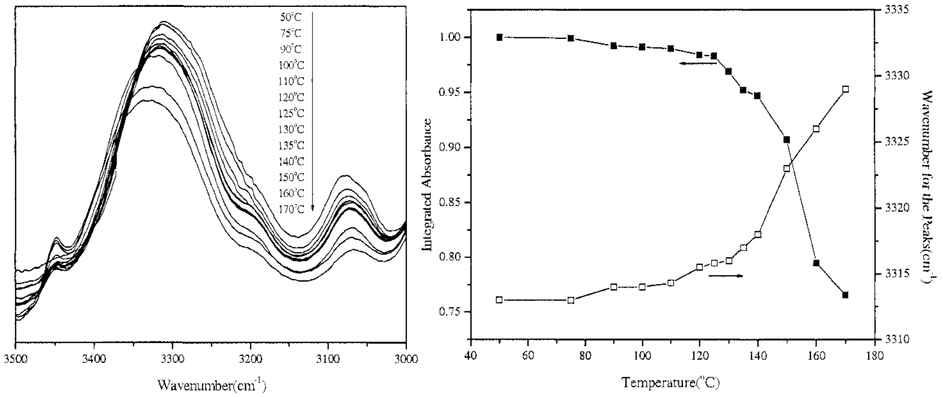

Figure 7. Infrared spectra of polyamide 12 16 at 3500-3000cm^{-1} region

Real-time FTIR has also been recorded for polyamides 10 16 and 8 16. The results are both accordant with the WAXD measurements for melt-crystallized samples of nylons 10 16 and 8 16. Figure 8 and 9 show the plots of variation of integrated absorbance taken as a function of temperature for nylons 10 16 and 8 16 respectively.

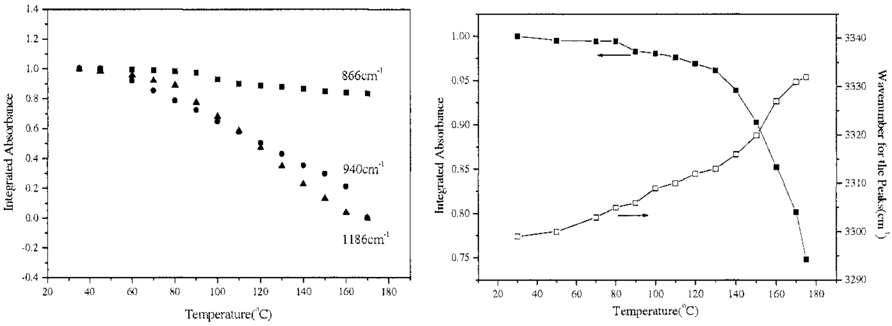

Figure 8. Variation of integrated absorbance with temperature for polyamide 10 16

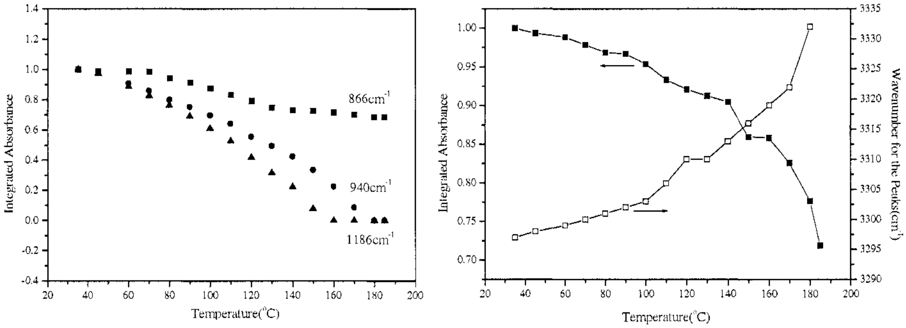

Figure 9. Plots of variation of integrated absorbance with temperature for polyamide 8 16

Skrovanek suggested that the shift of –NH– groups with temperature results from the variation of the hydrogen bond intensity [17,18]. In other words, with increasing temperature, the shift of free –NH– to hydrogen-bonded –NH– is so insignificant that the amount of hydrogen-bonded –NH– groups almost remains. Nevertheless, the strength of hydrogen bond decreases upon heating. Furthermore, the integrated absorbance of –NH– groups of polyamides decreases dramatically around the Brill temperature, while the frequency of peak increases distinctly. Based on the forementioned discussion, such a weakening of hydrogen bond results from the 'local melting' [19-21] of methylene between amide groups during Brill transition. That is to say, the vibration amplitude of the atoms located at crystal lattice keeps on enhancing with increasing temperature until the local melting takes place. Then the crystals present a hexagonal symmetry along the projection of the molecular chains after the □ structure has been destroyed. The reason why it is called pseudo-hexagonal phase comes from the fact that such a kind of hexagonal crystal structure cannot rotate around the central axis. It is the torsion caused by local melting of methylene groups that lessens the effect of hydrogen bond. Therefore, the strength of hydrogen bond declines during the crystalline transition.

Conclusion

Polyamides 12 16, 10 16 and 8 16 display different crystalline transition behaviors on heating investigated by variable-temperature WAXD. Both melt-crystallized samples and single crystals of nylon 8 16 show Brill transition before melting upon heating, while no crystalline transition is observed until melting in either melt-crystallized sample or single crystals for nylon 10 16. Interestingly, the crystalline transition behavior of nylon 12 16 is situated between those of nylon 8 16 and nylon 10 16, i.e., the Brill temperature of the melt-crystallized sample is lower than its melting point and the crystalline transition does not occur before melting on heating for single crystals. The variety in crystalline transition behavior of nylons studied in this work may result from the difference in arrangement of hydrogen bonds within the crystal due to the different lengths of alkane segments between amine groups and acid groups. Additionally, the real-time FTIR results are all consistent with those of variable-temperature WAXD measurements. A further consideration on the mechanism of the crystalline transition suggests that Brill transition originate from the 'local melting' of methylene between amide groups.

Acknowledgements. This work is subsidized by the Special Funds for Major State Basic Research Projects (G1999064802) and the National Natural Science Foundation of China.

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