Polymorphism of poly(nonamethyleneoxamide) crystal

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Abstract

The crystal structures of poly(nonamethyleneoxamide) (nylon-9,2) were investigated by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry. Nylon-9,2 shows a polymorphism with two different structures depending on the conditions of sample preparation. Monoclinic form I is the dominant crystalline phase for the solution-crystallized sample. For melt-crystallized samples, form I and new monoclinic form I′ coexist. Variable-temperature WAXD measurements were used to investigate the stability of each crystal form and the phase transition. Form I does not undergo any phase transitions prior to melting, although the orthorhombic molecular chain packing in form I at low temperature comes close to the quasi-hexagonal one during the heating process. Form I′ shows no phase transition on heating until its melting, too. The crystal lattice simply expands due to the thermal expansion. Form I is believed to be more stable, because the melting temperature of form I is higher than that of form I′.

Keywords: polyoxamide, polymorphism, crystal structure, wide-angle X-ray diffraction

1. Introduction

Polyoxamides (-NH-R-NH-CO-CO-) have excellent properties such as high melting points, high modulus, and low solubility in engineering plastics. In their molecules, oxamide groups consist of two amide bonds, therefore polyoxamides are classified as nylon-x,2 materials. The crystal structures of even and odd polyoxamides have been compared with even-even nylons and odd-even nylons, respectively.

The crystal structures for aliphatic nylons have been widely investigated [1-5]. Generally, the α form appears in the crystals of even-even nylons [1,6]. The crystal structure of the α form constructed by the stacking of the molecular sheets composed of hydrogen-bonded molecular chains in the fully extended planar zig-zag conformation. X-ray diffraction pattern of the α-form is characterized by two strong Bragg reflections that appear at *d*-spacings close to 4.4 and 3.8 Å. These *d*-spacings correspond to the inter-chain distances within and between the molecular sheets, respectively. For the odd-even and even-odd nylons, on the other hand, only the amide groups can partially establish hydrogen bonds within the molecular sheets. It was reported by Kinoshita [7] that these nylons seems to primarily crystallize into the γ-form, in which amide groups tilt with respect to the chain axis and form complete hydrogen bonds in the molecular sheets. While, the existence of the crystalline phase similar to the α-form have been reported for various aliphatic nylons containing methylene segments with odd numbers, such as nylon-5,6 [8,9], nylon-5,10 [10], nylon-9,2 [11], nylon-6,5 [12], nylon-12,5 [13], and even-odd nylons derived from undecanedioic acid [14]. The wide-angle X-ray diffraction (WAXD) patterns of these nylon crystals give two strong Bragg reflections at *d*-spacings ca. 4.4 and 3.7 Å, which are similar to those of the α-form of even-even nylons [1,2].

In the case of even polyoxamides, the crystal structures of nylon-4,2 [15], nylon-6,2 [16,17] nylon-8,2 [16], nylon-10,2 [16], and nylon-12,2 [16,18] were studied by means of wide-angle X-ray diffraction (WAXD). The WAXD patterns of the crystals of these polyoxamides show two characteristic Bragg reflections at *d*-spacings of 4.5 and 3.7 Å, similar to the α-form of even-even nylons. While for odd polyoxamides, only the crystal structure of nylon-9,2 has been determined by using the X-ray fiber diffraction pattern [11]. The typical *d*-spacings of the α-form are found in the WAXD pattern of nylon-9,2 crystal despite of odd-even nylon. We call here this crystalline phase of nylon-9,2 “form I”. Figure 1 shows the crystal structure of form I of nylon-9,2 reported by Franco, et al [11]. In form I of nylon-9,2, the chains are in all-trans conformation, and the torsion angle C(O)-N(H)-C(H_2)-C(H_2) is about 155°, which allows hydrogen bonds between neighboring chains to be formed. Consecutive oxamide planes (-NH-CO-CO-NH-) tilt out of the plane in opposite senses and form two types of hydrogen bonds in different directions. As a result, nylon-9,2 shows an orthorhombic molecular chain packing in form I (Fig. 1(a)).

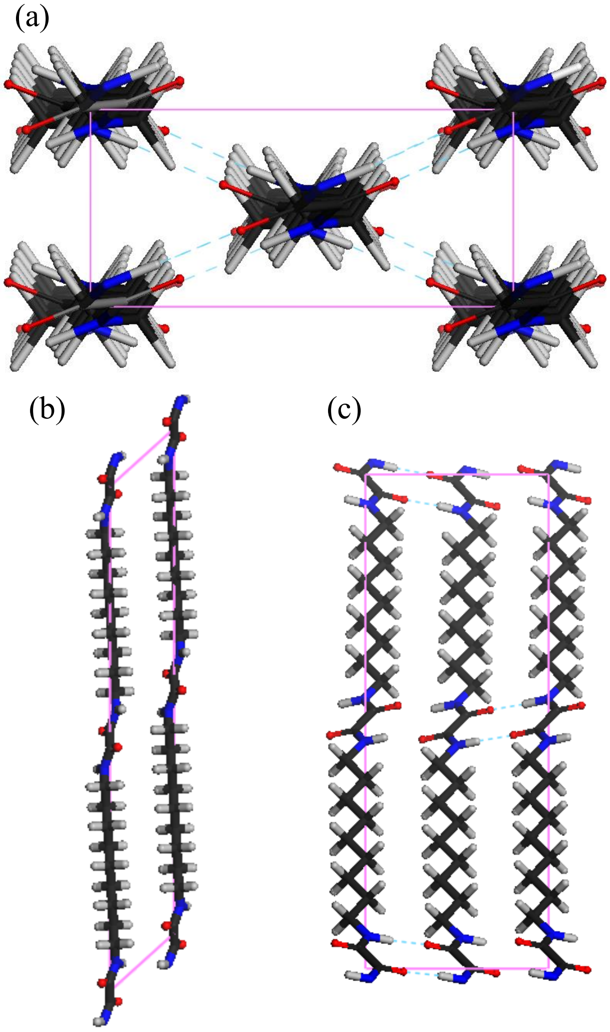

Figure 1. Crystal structure of form I of nylon-9,2 reported by Franco, et al [11]. (a) Projection along the *c*-direction, (b) Projection along the *b*-direction. (c) Projection along the *a*-direction. Solids pink lines indicate the unit cell and hydrogen bonds are indicated by dashed lines. Color code: nitrogen: blue; oxygen: red; carbon: black; and hydrogen: gray. Orthorhombic molecular chain packing in the *ab*-plane can be found in (a).

As noted above, it have been reported that nylon-9,2 crystallizes into the α-like form (which we call form I) in spite of odd-even nylon [11]. Generally, other odd-even nylons have another crystalline form, the γ-form. The existence of neither the γ-form or other polymorphs have been reported for nylon-9,2. The aim of this study is to investigate the polymorphism of nylon-9,2. In this study, we prepared the oriented fiber, solution-crystallized, and melt-crystallized samples. The crystal structures of the nylon-9,2 samples are investigated by WAXD and differential scanning calorimetry (DSC). Firstly, we will confirm that only form I exists in the oriented fiber sample as previously reported [11]. Then, we will show that nylon-9,2 crystal have a new crystalline phase which is different from form I (α-like form) for both solution-crystallized and melt-crystallized samples. The crystal structures of the polymorphs of nylon-9,2 and their temperature dependence will be discussed.

2. Experimental

2.1. Synthesis and preparation

Nylon-9,2 was synthesized by polycondensation of 1,9-nonamethylenediamine and dibutyl oxalate according to the two-step synthesis method previously reported [11,16]. 1,9-nonamethylenediamine and dibutyl oxalate were supplied from Ube Industries, Ltd (Ube, Japan) and Kuraray Co. Ltd (Tokyo, Japan), respectively. The intrinsic viscosity of the polymer was determined using an Ubbelohde viscometer in sulfuric acid (96% wt/wt) at 25 ± 0.1 °C, and was determined as 1.23 dL/g. The synthesized polymer was dried at 110 °C for 12 h in a vacuum and used for sample preparation or measurements.

A sheet with 1 mm thickness was prepared by compressing the molten polymer at 280 °C and then immediately quenching it in an ice-water bath. The sheet was elongated to 200% of its initial length at 200 °C and annealed at the same temperature for an hour in order to give the oriented fiber sample. The solution-crystallized sample (SCS) was obtained from dilute solution (0.05% (w/v)) in 1,4-butanediol. The polymers were dissolved in the solvent at 200 °C and crystallized at 150°C for 2 h. The melt-crystallized sample (MCS) was prepared at 235 °C for 24 h in a glass tube with a diameter of 5 mm.

2.2. WAXD measurement

WAXD patterns of a fiber sample were recorded on cylindrical films for 12 h at room temperature. Ni-filtered Cu-Kα radiation (wavelength λ = 1.542 Å) from an X-ray generator (Rigaku RAD IA) operating at 35 kV and 20 mA was used. The camera diameter (R = 35.01 mm) was calibrated from the Bragg peaks of Si standard powder.

WAXD patterns of the SCS and MCS were recorded for 5 min using Bruker AXS DIP220 with monochromatic Cu-Kα radiation (40 kV, 250 mA). A two-dimensional detector (imaging plate system) was used. The sample was held in the sample holder of a copper-block furnace and covered with polyimide films. The temperature of the sample was controlled with a PID controller within ±0.1 °C. WAXD patterns were recorded on the imaging plate with an exposure time of 5 min at different temperatures. The intensity-2θ profiles were obtained from the two-dimensional WAXD profiles.

2.3 Differential Scanning Calorimetry

The thermal behavior of MCS was investigated by differential scanning calorimetry (DSC) with Rigaku DSC8320 apparatus at a scanning rate of 10 °C/min in nitrogen atmosphere.

A small amount of sample (1.5‐2 mg) was used for the DSC measurements. The temperature of the calorimeter was calibrated using the melting temperature of an indium standard.

3. Results and Discussion

3.1. WAXD pattern of the oriented fiber sample

The WAXD pattern of the oriented fiber sample was measured to investigate the crystalline form. Figure 2 shows the observed WAXD pattern of the oriented fiber of nylon-9,2. Two intense Bragg reflections are found at *d*-spacings of 4.21 Å and 3.63 Å (reflection peaks 3 and 6, respectively) on the equatorial line. These *d*-spacings are typical for α-form of even-even nylon. Furthermore, a strong Bragg spot appears at a *d*-spacing of 11.46 Å. These three reflections were also confirmed by previous WAXD measurement of the oriented fiber sample of nylon-9,2 [11]. Therefore, it is concluded that the fiber sample prepared in this study is also in form I similar to that prepared by Franco, et al. The observed *d*-spacings (d_{obs}s) of the Bragg reflections are listed in Table 1. The reflections are initially indexed by using the monoclinic unit cell parameters determined in previous work [11] as listed in Table 1. The lattice constant is determined using the d_{obs}s as a = 5.29 Å, b = 8.56 Å, c = 29.54 Å, β = 50 .9°; these values are approximately the same as those reported in previous work by Franco, et al [11]. The d_{obs} values nearly agree with the calculated *d*-spacings (d_{cal}s) using the determined lattice constants listed in Table 1. Extinction condition for space group *C*2/*c* determined by Franco, et al. is also conformed. Therefore, it is concluded that only form I exist in the oriented fiber sample.

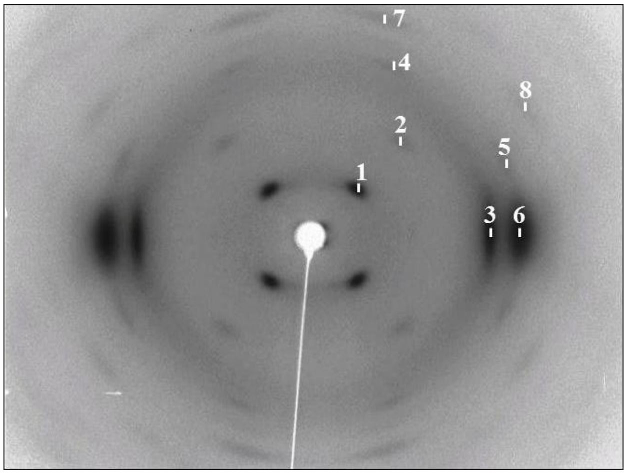

Figure 2. WAXD pattern of the oriented fiber of nylon-9,2. Eight major Bragg reflections numbered 1-8 are observed and listed in Table 1.

Table 1 Observed and calculated *d*-spacings of the nylon-9,2 oriented fiber. Abbreviations denote intensities: s: strong and m: medium.

No.	d_{obs} / Å	d_{cal} / Å	Index
1	11.46 s	11.46	0 0 2
2	5.76 m	5.73	0 0 4
3	4.21 s	4.28	0 2 0
4	4.05 m	4.05	1 1 6
5	3.85 m	3.73	0 2 3
6	3.63 s	3.70	1 1 0
7	3.30 m	3.38	1 1 8
8	3.14 m	3.13	0 2 5

3.2. WAXD patterns of the SCS and MCS

Figure 3(a) shows the WAXD pattern of the SCS. The intense three Bragg reflections are observed at $2\theta = 7.92°$ (S1), 20.85° (S2), and 24.66° (S3). The *d*-spacings of them are 11.16 Å, 4.26 Å, and 3.61 Å, which approximately correspond to the *d*-spacings of the 002, 020, and 110 Bragg reflections of form I, respectively. Therefore, the main crystalline phase of the SCS is considered to be form I. These reflection data are listed in Table 2. Reflections S′1, S′2, and S′3 in Fig. 3(a), which cannot be indexed as form I, are also observed for the SCS. According to the previous study [11], the authors pointed out that the reduced number of chain repeat units in the lamellar thickness may contribute to the reflection S′1. It is therefore not a Bragg reflection peak. We believe that reflections S′2 and S′3 around the 020 reflection of form I are identified as amorphous halo and Bragg reflection of different crystalline form, as will be discussed later.

Figure 3(b) shows the WAXD pattern of the MCS, which is clearly different from that of the SCS. Observed Bragg reflections are listed in Table 2. The observed *d*-spacings were calculated using the peak positions of Bragg reflections obtained by peak separation of the WAXD pattern. Reflections M2, M5, and M9 in Fig. 3(b) are identified as the 002, 020, and 110 reflections of form I, respectively. However, the reflections except M2, M5, and M9 cannot be indexed by using the lattice parameters of form I. This result indicates that additional crystalline form, other than form I, crystallize in the MCS. Although the detail will be shown later, this additional crystalline phase is defined as form I′ in this study.

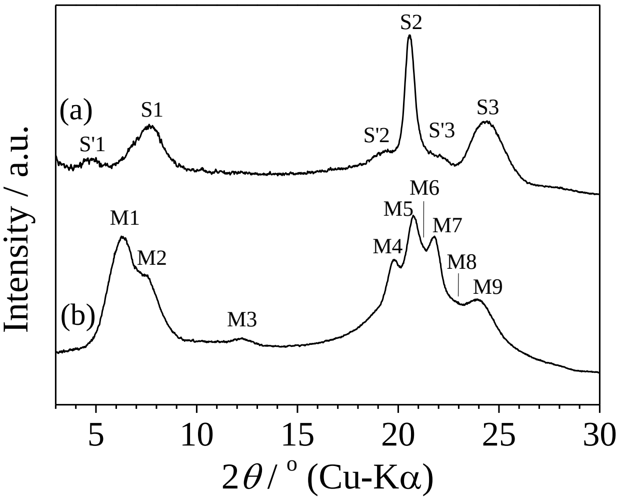

Figure 3. WAXD patterns of (a) the SCS and (b) the MCS of nylon-9,2 at 25 °C.

Table 2 Observed *d*-spacings for the two nylon-9,2 samples: the solution-crystallized sample (SCS) and the melt-crystallized sample (MCS)

SCS				MCS			
Reflection No.	d_{obs} [Å]	*hkl*	Crystalline phase	Reflection No.	d_{obs} [Å]	*hkl*	Crystalline phase
				M1	14.47		Form I′
S1	11.16	0 0 2	Form I	M2	11.60	0 0 2	Form I
				M3	7.22		Form I′
				M4	4.49		Form I′
S2	4.26	0 2 0	Form I	M5	4.28	0 2 0	Form I
				M6	4.19		Form I′
				M7	4.07		Form I′
				M8	3.91		Form I′
S3	3.61	1 1 0	Form I	M9	3.70	1 1 0	Form I

3.3. Temperature variation of the crystal structure in the SCS

The temperature variation of the crystal structure in the SCS is investigated by WAXD. Figure 4 shows the temperature dependence of the WAXD patterns of the SCS upon heating. The peak position of the 002 reflection of form I does not change until melting. While, the 020 and 110 reflection peaks shift to higher scattering angle and the lower scattering angle, respectively. Temperature dependences of the *d*-spacings, d_{020} and d_{110}, of the SCS are shown in Fig. 5. As temperature rises, d_{020} decreases. While, d_{110} increases with an increase in temperature. The changes in the *d*-spacings show that the orthorhombic molecular chain packing in form I at low temperature comes close to the quasi-hexagonal one at high temperature.

Above behavior of the molecular chain packing is often observed for other nylon below the Brill transition. On heating, the crystalline phase transition, the so-called Brill transition, is observed in aliphatic nylons [4,5,19,20]. The Brill transitions of various nylons have been extensively studied [21-23]. X-ray diffraction is the most useful technique to confirm this transition. The two strong reflections at *d*-spacings of 4.4 and 3.7 Å merge into a single peak at the Brill transition. According to a conformational study on the transition, the mobility of the methylene segments between the amide groups increases at the Brill transition, although the hydrogen bonds between the neighboring chains are maintained [24,25]. As a result, the packing of the molecular chains changes from triclinic or orthorhombic to quasi-hexagonal.

In present case, the 020 and 110 reflections do not merge into a single peak before melting. Thus, it is concluded that form I crystal of the nylon-9,2 does not undergo the Brill transition. This experimental fact has been already reported by Franco and coworkers [11]. According to them, the hydrogen bonds in two directions at an oxamide group between nylon-9,2 molecules seem to make difficult to occur the Brill transition. The reflections S′2 and S′3 belonging to form I′ in Fig. 3 shift to lower scattering angle with an increase in temperature and vanish at 250 °C. The behavior detail of the reflections belonging to form I′ will be discussed later (in the MCS section).

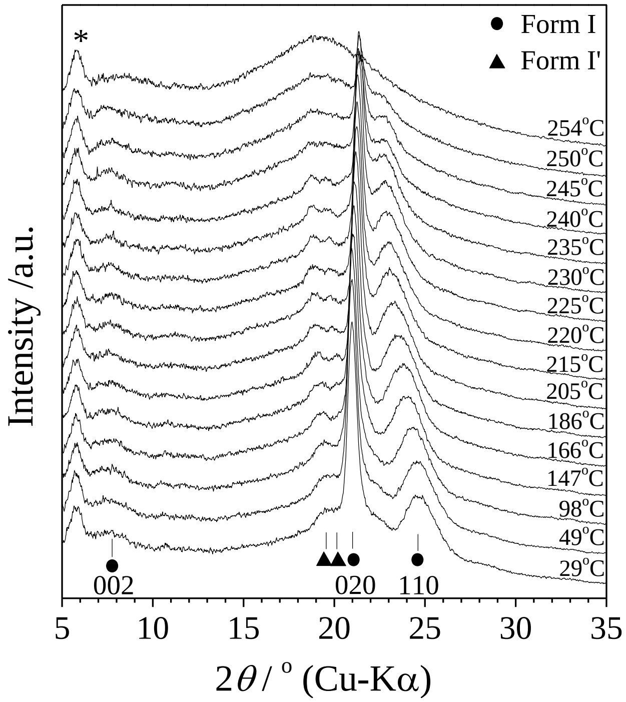

Figure 4. The temperature dependence of WAXD pattern of the SCS of nylon-9,2 on heating process. The reflection peak (*) corresponds to that of polyimide film.

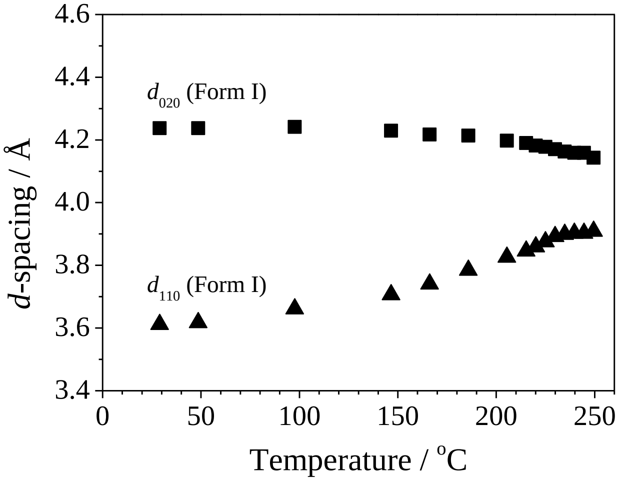

Figure 5. Temperature variations of *d*-spacings of the SCS sample of nylon-9,2 during the heating process.

re in the MCS

Figure 6 shows the temperature variation of the WAXD pattern of the MCS. The reflection peaks at $2\theta = 7.0°$, 20.80°, and 23.96° in the WAXD pattern at 25°C can be assigned the 002, 020, and 110 reflection of form I, respectively. These reflections correspond to the M2, M5, and M9 reflection peaks in Fig. 3(b). The temperature variations of the peak positions of these reflections are consistent with those of the SCS shown in Fig. 4.

The reflection peaks at $2\theta = 6.37°$, 12.26°, 19.82°, 21.20°, 21.84°, and 22.80° in the WAXD pattern at 25°C in Fig. 6, which correspond to the M1, M3, M4, M6, M7, and M8 reflection peaks in Fig. 3(b), respectively, are considered to be identified as the Bragg reflections of form I′. The peak M1, which is expected to relate to the fiber period ($00l$), shifts to a higher scattering angle with an increase in temperature. On the other hand, the M3, M4, M6, and M7 reflection peaks, which are expected to be from the lateral packing of the molecules, shift to lower scattering angles. At 245°C, the M1, M3, M4, M6, M7, and M8 reflection peaks disappear simultaneously; this means that these peaks belong to same crystalline phase, form I′. While, the reflection peaks of form I begin to disappear at 254°C. Solid-solid phase transition between forms I and I′ is not observed. Thus, it is concluded that the new form I′ is found for the MCS, and the melting temperature of form I′ is lower than that of form I. The latter fact suggests that form I is more stable than form I′.

Figure 7 shows the temperature dependences of the *d*-spacings observed for the MCS. The temperature dependences of the *d*-spacings of M5 and M9, which are d_{020} and d_{110} of form I, are same as those observed for the SCS. The tendency of the change of the molecular chain packing in form I from orthorhombic to quasi-hexagonal is confirmed also for the MCS. It should be noted that the d_{020} and d_{110} of form I in the MCS are larger than those in the SCS, but the reason have not been cleared, yet. On the other hand, all the *d*-spacings of form I′ (M4, M6, M7, and M8) continuously increase with an increase in temperature; the molecular chain packing in form I’ becomes loose due to the thermal expansion.

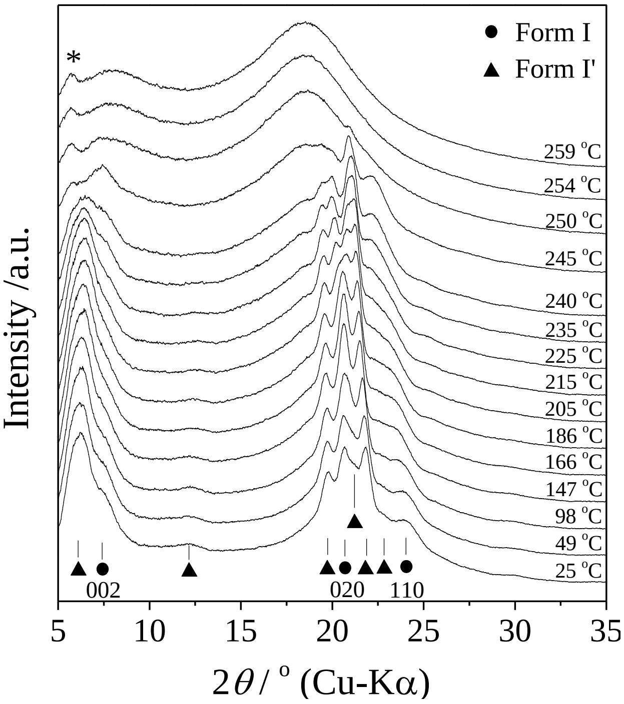

Figure 6. The temperature dependence of XRD pattern of the MCS sample of nylon-9,2 on the heating process. The reflection peak (*) corresponds to that of polyimide film.

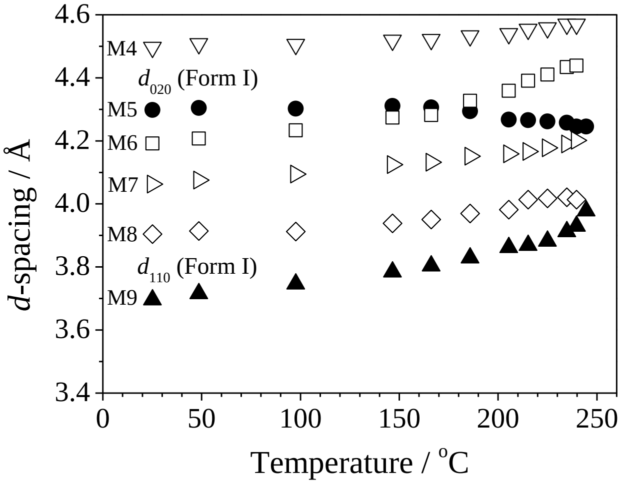

Figure 7. Temperature variations of *d*-spacings of the MCS of nylon-9,2 during the heating process.

Figure 8 shows the DSC heating curve of the MCS of nylon-9,2. The initial sample was crystallized at 235 °C for 24 h. Three endothermic peaks are observed at 235 °C, 244 °C, and 252 °C. The endothermic peaks at 245 °C and 252 °C is considered to be the melting peaks of form I′ and form I, respectively. It should be noticed that the small endothermic peak at 235 °C is broad. The temperature variation of WAXD pattern of the MCS showed no polymorphic transition on heating process. In the case of crystalline polymers, small crystals formed during the cooling after the isothermal crystallization. Therefore, the small endothermic peak at 235°C is probably due to the melting of small crystallites.

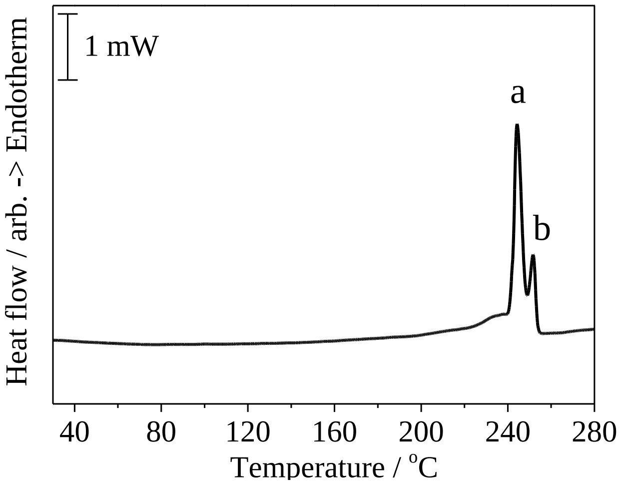

Figure 8. DSC heating curve of melt crystallized sample (MCS) of nylon-9,2. The peaks a and b is expected to correspond to the melting of form I′ and form I, respectively.

3.5. Crystal structure of form I′

As mentioned above, it was found that nylon-9,2 crystal shows the polymorphism; form I and form I′ appear depending on crystallization condition. Polymorphism is often observed in other nylon materials as well as nylon-9,2. For example, the α-like form and γ-form are observed for odd-even nylons. It has been reported that nylon-5,10 shows a polymorphism depending on the conditions of sample preparation [10]. Nylon-5,10 had an α-like structure when the sample was prepared from strong acid solutions or their mixture with chloroform. While, the γ-form crystallizes from the melt. Nylon-9,2 may pack in the same manner to the γ-form, and should give rise to a Bragg reflection around *d* = 4.15 Å which is peculiar to the γ-form crystal. However, the WAXD patterns of form I and form I′ are clearly different from the WAXD pattern of the γ-form. The torsion angle 120° of the NH-CH$_2$ bond is required for the γ-form. The higher conformational rigidity of the oxamide groups than amide groups may cause the absence of the γ-form for nylon-9,2.

In some aliphatic nylons, a high-temperature form is observed. For example, the high-temperature form of nylon-5,6 has been found by Puiggalí, et al [8]. Nylon-5,6 crystallized from a solution has a monoclinic structure, where hydrogen bonds are formed along two directions the same as form I of nylon-9,2. This form undergoes the Brill transition involving a structural change to a quasi-hexagonal packing on heating. On successive heating, a new crystalline phase with monoclinic structure appears at a temperature a few degrees below the melting point. This high-temperature form is also found for nylon-5,6 crystallized from the melt. Characteristic Bragg reflections are observed at *d* = 4.54 Å, ~~and~~ 4.36 Å, and 4.23 Å in the WAXD pattern of the high-temperature form at 220 °C. These two reflections cannot be assigned to the reflection peaks of the γ-form. A monoclinic unit cell with $\beta \neq 90°$ was determined for the high–temperature form from X-ray fiber diffraction patterns at 220 °C. The unit cell of the high-temperature form is related to that of the low temperature form taking into account a slight change in the angle between the two hydrogen bond directions and thermal expansion.

In the case of nylon-9,2, form I′ shows characteristic reflections at d = 4.49 Å, 4.19 Å, and 4.07 Å (see Fig. 3b) in the WAXD pattern at 25 °C. This suggests that the molecular packing of form I′ may be similar to that of the high-temperature form of nylon-5,6. In the WAXD pattern of the bulk sample, the reflection peak, which originates from fiber period of form I′ (and may be 002 (or 001) reflection), is detected at $2\theta = 6.22°$ (d = 14.19 Å). While, the 002 reflection of form I is observed at $2\theta = 7.61°$ (d = 11.60 Å) for the MCS. There are two possible interpretations of this difference. One is the difference in molecular conformation. The molecular chain in form I′ takes more extended conformation than that in form I. The chains has practically all-trans conformation, and the torsion angle C(O)-N(H)-C(H_2)-C(H_2) is about 155° in form I. A fiber period increases if the torsion angle becomes large with preservation of β angle. For example, fiber period reaches about 32 Å when the torsion angle is 180°. However, the 002 (or 001) reflection of form I′ suggests that lattice parameter c is 37.4 Å, which is larger than 32 Å. Therefore, it is likely that the larger d_{002} in form I′ is not expected by the extended conformation of molecules.

The other interpretation is difference in molecular arrangement. The unit cell parameter β becomes large for form I′ in the case that the relative molecular position along the chain axis between neighboring chains is different from that in form I, which is caused by the hydrogen bond geometry. In this case, we obtain a monoclinic unit cell with a = 4.73 Å, b = 8.96Å, c = 29.54 Å, and β = 76.7°, assuming that the lattice constant c of form I is preserved. The unit cell parameters enable us to index the observed Bragg reflections of form I′. Finally, a tentative lattice constant of form I′ is refined using the observed d-spacings (d_{obs}s) and determined to be a = 4.83 Å, b = 8.97 Å, c = 30.64 Å, and β = 70.9°. The d_{obs} values nearly agree with the calculated d-spacings as listed in Table 3.

Table 3 Observed and calculated *d*-spacings for form I′ of nylon-9,2.

Index	d_{cal} [Å]	d_{obs} [Å]
0 0 2	14.48	14.47
0 0 4	7.24	7.22
0 2 0	4.49	4.49
1 1 1	4.20	4.19
1 1 0	4.07	4.07
$\bar{1}$ 1 1	3.88	3.91

Moreover, form I′ is less stable than form I and shows temperature variation owing to thermal expansion on heating. Hence, the crystal structure in form I′ is disordered, and molecules in form I′ have many defects. The disordered molecular structure in form I′ may cause the stretching the fiber period. Furthermore, the molecular conformation containing defects in form I′ requires the different packing of the chains and the different hydrogen bonding system from those in form I.

4. Conclusions

We have investigated the polymorphism of nylon-9,2. Two different crystal structures are confirmed by WAXD. One is monoclinic form I, which is previously reported and has α-like structure, where hydrogen bonds are formed along two directions. The other is new form I′ found in this study. When nylon-9,2 is crystallized from the solution, form I dominantly appears. While, in the case of melt-crystallized nylon-9,2, form I and form I′ coexist. The temperature variations of the WAXD patterns shows that both forms do not undergo any phase transitions until their melting and that the melting of the form I′ crystal begins at a lower temperature than that of form I. These facts suggest that the form I′ is a metastable phase. It is considered from the WAXD pattern that crystal structure of form I′ is disordered compared to that of form I.

Acknowledgments

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