



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'.

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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 seem 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”. Fig. 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(H₂)–C(H₂) is about 155°, which allows hydrogen bonds between neighboring chains to be

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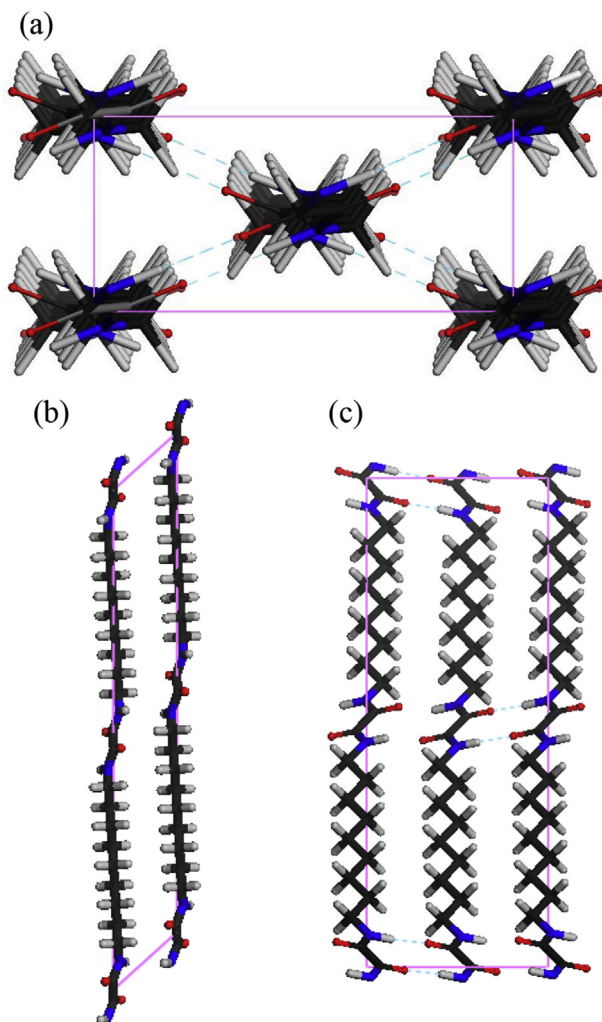


Fig. 1. Crystal structure of form I of nylon-9,2 reported by Franco et al. [11]. (a) Projection along the *c*-direction, (b) Projection along the *b*-direction. (c) Projection along the *a*-direction. Solids pink lines indicate the unit cell and hydrogen bonds are indicated by dashed lines. Color code: nitrogen: blue; oxygen: red; carbon: black; and hydrogen: gray. Orthorhombic molecular chain packing in the *ab*-plane can be found in (a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

formed. Consecutive oxamide planes ($-\text{NH}-\text{CO}-\text{CO}-\text{NH}-$) 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)).

As noted above, it has 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 has 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-K α radiation (wavelength $\lambda = 1.542$ 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-K α 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. Fig. 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

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