Note

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ELECTRON MICROSCOPIC OBSERVATION ON THE MATERIAL TRANSFORMED FROM THE SINGLE CRYSTAL OF *p*-AMINOHIPPURIC ACID THROUGH THE THERMAL SOLID STATE POLYCONDENSATION PROCEDURE

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ABSTRACT: Morphological change in a product from *p*-aminohippuric acid monomer single crystal through the thermal solid state polycondensation reaction at 170 °C up to 1200 h is observed mainly by means of scanning electron microscopy. In the early stage of the polymerization process (100–200 h), many rectangular prisms ca. 5 μm long are observed on the surface of the specimen. A needle-shaped or fibrillar material is formed after the polymerization for ca. 250 h. It is found that the surface of the specimen is finally covered with the microfibrils ca. 100 nm in diameter.

1. INTRODUCTION

Several crystalline polyamides are known to be produced from single crystals of the monomers through the thermal solid state polycondensation procedure [1,2], an example of which is the biaxially oriented nylon 6 crystal formed by the heat treatment of the single crystal of ϵ -n-aminocaproic acid [3,4]. We have reported similar results for two types of ω -amino acids [5–7]: glycine is converted into the type-I crystal of polyglycine and β -alanine changes to the type-I modification of nylon 3 crystal by annealing the monomer single crystals for a long time at temperatures below melting points of the crystals. It was also reported in our previous paper [8] that the single crystal of *p*-aminohippuric acid (*p*-AHA) can be converted into the polymer crystal by a similar polymerization technique in the solid state.

In this study, morphological change in the specimen through the polycondensation reaction is observed mainly by scanning electron microscopy (SEM), confirming the chemical structure of the polymerized material.

2. EXPERIMENTAL

5 g of the commercial *p*-AHA (Nakarai Tesque, Inc.) was dissolved in 650 mL of the mixed solvent of etha-

nol and water (2:8) at 80 °C, and recrystallized at 30 °C from the solution. The single crystals obtained were ca. 1–10 mm in size and used as the original specimens or the starting material for the polymerization.

Such specimens were polymerized at 170 °C in the evacuated glass tube immersed in a silicone bath. The longest term of polymerization was 1200 h in this study. Change in the morphology of the specimen during the heat treatment was examined in a Hitachi 410 SEM with an accelerating voltage of 5 kV after being coated with gold. The X-ray diffraction photographs were taken with a flat camera mounted on an X-ray generator (Rigaku, Cat. No. 4001A) with Ni-filtered CuK α radiation.

3. RESULTS AND DISCUSSION

It was firstly confirmed from the results obtained by infrared spectroscopy and differential thermal analysis that an aromatic polyamide was produced from *p*-AHA during the heat treatment. A possible reaction process is suggested in Fig. 1.

Fig. 1. A scheme for the conversion process from *p*-AHA into poly (*p*-AHA) in the solid state.

Fig. 2. A photograph of the single crystals of *p*-AHA.

Fig. 3. X-ray diffraction patterns taken from three types of specimens; (a) the single crystal of *p*-AHA, (b) polymerized for 120 h, (c) polymerized for 260 h.

Fig. 4. A scanning electron micrograph of the surface of *p*-AHA monomer single crystal.

Fig. 5. A scanning electron micrograph of the surface of the specimen annealed for 80 h.

It was found that the single crystals of *p*-AHA precipitated from the solution continued to grow gradually at 30 °C during ca. 1 week. Aggregated single crystals of *p*-AHA recrystallized from the solution are shown in Fig. 2. Each monomer single crystal is transparent and needle- or prism-shaped, the size of which is on the order of 1 - 10 mm.

X-ray diffraction photographs taken from three types of specimens are shown in Fig. 3. Laue spots were recorded from the single crystal of *p*-AHA (Fig. 3-a), while Debye-Scherrer rings reflected from the polymerized crystallites appear with the original Laue spots in the case of the specimen annealed for 120 h (Fig. 3-b). Debye-Scherrer rings are only observed for

Fig. 6. A scanning electron micrograph of the surface of the specimen annealed for 150 h.

Fig. 8. A scanning electron micrograph of the surface of the specimen annealed for 1200 h.

Fig. 7. A scanning electron micrograph of the surface of the specimen annealed for 260 h.

the sufficiently polymerized specimen (annealed for 260 h) as shown in Fig. 3-c, where a slight degree of orientation for the polymer crystal is suggested by careful observation of the diffraction rings.

A SEM photograph of *p*-AHA single crystal is shown in Fig. 4, from which the crystal surface appears to be very flat or any characteristic structure is not observed with this magnification.

In the early stage of the polymerization process (several tens of hours of annealing), rectangular laminal materials begin to emerge on the surface of the specimen as shown in Fig. 5. The polycondensation reaction in the solid state seems to initiate in such areas. Numerous rectangular prisms are observed over the surface of the specimen after the heat treatment for 100 - 200 h as shown in Fig. 6.

The size of each prism was estimated to be on the order of $5 \times 0.5 \times 0.5 \mu\text{m}^3$. Such a prism-shaped morphology was also found in the early stage of polycondensation processes from glycine and β -alanine single crystals [5,7]. Needle-shaped or fibrillar material was yielded on the specimen surface after the polymerization of ca. 260 h as shown in Fig. 7. Each fibril looks thinner than the rectangular prism in Fig. 6. Such fibrillar material is considered to originate from the prism-shaped one and seems to be mainly composed of poly(p -AHA). In the final stage of the reaction (annealing for 1200 h), surface of the specimen was covered with aggregated fibrillar materials as shown in Fig. 8-a. It is estimated from Fig. 8-b, a micrograph with higher magnification than Fig. 8-a, that each fibril is ca. 100 nm in diameter. In comparison with the results obtained from the solid state polycondensations of glycine and β -alanine [5,7], it is reasonably suggested that such a fibrillar structure corresponds to the final morphology of the material

with the complete polymerization.

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MORPHOLOGICAL STUDY ON CARBON FIBERS AND FILMS DERIVED FROM POLYOXADIAZOLE

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ABSTRACT: For carbons derived from polyoxadiazole, the effects of macroscopic geometry of starting materials on the formation of microtextures of resulting carbons have been studied in relation with processing factors by scanning electron microscopy.

1. INTRODUCTION

Among a number of polymers, polyoxadiazole (POD) is of special interest in giving graphitizable carbon [1]. POD-based carbon heat-treated at high temperature shows a higher electric conductivity than other carbons derived from other heat-resistant condensation polymers [2].

The present authors investigated previously the structure of POD-based carbon fibers in relation to preparation conditions of starting POD fibers [3]. In this paper, the effects of macroscopic specimen geometries on the development of microtextures of POD-based carbons are studied.