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Preparation of needle-like poly(azomethine) crystals by means of reaction-induced crystallization of oligomers

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Abstract

Needle-like poly(azomethine) crystals were successfully prepared by the polycondensation of 1,4-phenylenediamine and 1,4-terephthalaldehyde in liquid paraffin at 180 °C. The favorable polymerization concentration for the preparation of the well-defined needle-like crystals was 2.0×10^{-2} mol l^{-1}. The average length and width of the needle-like crystals were 7.7 and 0.6 μm, respectively. These crystals possessed high crystallinity and good thermal stability. The extended polymer chains were aligned along the long axis of the needle-like crystal. The morphological observations indicated that the needle-like crystals were formed through the spiral growth of the oligomer lamellae caused by the screw dislocation.

Keywords: Needle-like crystals; Polycondensation; Poly(azomethine)

1. Introduction

Aromatic poly(azomethine)s belong to a class of high performance materials that are known because of their excellent thermal stability, good mechanical properties and environmental resistance, [1–4] but more particularly as promising materials with optoelectrical, photonic and magnetic application [5–8]. Numerous types of poly(azomethine)s have been synthesized by the condensation reaction between aromatic dialdehydes and diamines. However, the high melting points and low solubility usually make them inaccessible for processing by conventional techniques. In order to improve their intractability, several approaches such as the introduction into the main chain of flexible aliphatic segments, bulky lateral substituents or fluorine groups have been attempted so far [9–12].

We have been studying on the morphology control of intractable polymers during solution polymerization, and succeeded in preparing the whiskers of poly(*p*-oxybenzoyl) (POB) and other aromatic polyesters by polymerization in liquid paraffin (LPF) [13–18]. These whiskers are formed by the reaction-induced crystallization of oligomers during solution polymerization. The polymer chains are aligned along the long axis of the whiskers. The formation mechanism of these whiskers was proposed as follows. When the degree of polymerization of the oligomers exceeded a critical value, they are precipitated from the solution to form lamellae. The lamellae piled up in the form of needle-like crystals with spiral growth. Post-polymerization occurred topochemically in the needle-like crystals, and the whiskers consisting of high molecular weight extended polymer chains were eventually formed [14]. The reaction-induced crystallization of oligomer is a very valuable method for the morphology control of intractable polymers to overcome the antagonistic problem between intractability and properties.

Recently, we have studied the morphology of poly(azomethine) by means of the reaction-induced crystallization of oligomer, and prepared the star-like aggregates of the cone-shaped crystals using the self-polycondensation of 4-aminobenzaldehyde [19]. This result shows that the morphology of poly(azomethine) crystals can also be controlled by the reaction-induced crystallization during polymerization. This article describes our new finding on the preparation of needle-like poly(azomethine) (PAZM) crystals prepared by the bimolecular polycondensation between 1,4-phenylenediamine (PPDA) and 1,4-terephthalaldehyde (TPA).

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2. Experimental

2.1. Materials

PPDA was a gift from Daishin Kasei Kogyo Co. Ltd and used as received. TPA was purchased from Tokyo Kasei Co. Ltd and used as received. LPF was purchased from Nacalai Tesque Co. Ltd and purified by vacuum distillation (220–240 °C/0.3 mmHg).

2.2. Polymerization

Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed 0.130 g of PPDA (1.20 mmol) and 60 ml of LPF. The reaction mixture was heated up to 180 °C under a slow stream of nitrogen with stirring. When PPDA was completely dissolved at ca. 150 °C, 0.161 g of TPA (1.20 mmol) was added into the solution. The stirring was stopped after TPA was completely dissolved. Reaction temperature was maintained at 180 °C for 5 h. The precipitated PAZM crystals were collected by vacuum filtration at 180 °C, and washed with *n*-hexane and acetone.

2.3. Characterization

Morphology of the products was observed on SEM (Hitachi S-2150). WAXS was conducted on a Rigaku 4012K2 with nickel-filtered Cu Kα radiation (35 kV, 20 mA). The electron diffraction was performed on TEM (Hitachi HU-200E). IR measurement was performed on JASCO FT-IR 350. Thermal properties were evaluated by DSC (Perkin–Elmer DSC-7) with a scanning rate of 10 °C min^{-1} in nitrogen atmosphere. Thermal stability was measured on TGA (Perkin–Elmer TGA 7) at a heating rate of 20 °C min^{-1} in nitrogen atmosphere.

3. Results and discussion

LPF is a poor solvent for not only the polymers but also PPDA and TPA. The condensation reaction between PPDA and TPA starts at ca 100 °C with the elimination of by-produced water. When both PPDA and TPA were placed into the reaction vessel, the precipitation of oligomers occurred before the monomers were completely dissolved. In this case, undissolved monomers acted as the nuclei, and therefore the crystals having clear habit were not obtained. In order to crystallize the oligomers in the homogeneous solution, TPA was added after PPDA was completely dissolved at 150 °C. The solution became turbid in a few minutes after the addition of TPA due to the precipitation of the oligomers. When the polymerization was carried out at 180 °C, the needle-like crystals were obtained as shown in Fig. 1. The favorable polymerization concentration for the preparation of the well-defined needle-like crystals was 2.0×10^{-2} mol l^{-1}. The needle-like crystals are grown from the center points, of which the average length is 7.7 μm. The average width of the middle part of the crystal is 0.6 μm, and it decreases from the center to the tip. PAZM crystals prepared by the self-polycondensation of 4-aminobenzaldehyde were the star-like aggregates of the cone-shaped crystals, of which the average length is 0.6 μm [19]. Compared with this, the length of the needle-like crystals prepared in this study is much longer. Aromatic rigid-rod poly(azomethine)s are generally dissolved into only concentrated sulfuric acid [1,2]. However, the obtained crystals were insoluble even in concentrated sulfuric acid, and therefore the chemical structure of the crystals could not be analyzed by NMR. FT-IR was measured to confirm the formation of PAZM. Fig. 2 shows the IR spectra of PPDA, TPA and the crystals. N=CH of azomethine groups appeared newly at 1617 cm^{-1} in the spectrum of the crystals. Both N–H of amino groups at 3420–3250 cm^{-1} of PPDA, and C=O of formyl groups at 1662 cm^{-1} of TPA decreased significantly. However, they did not disappear completely in the spectrum of the needle-like crystals even though the peak intensities were small. This result shows that poly(azomethine) is synthesized in the form of the crystals, but the molecular weight is not quite high.

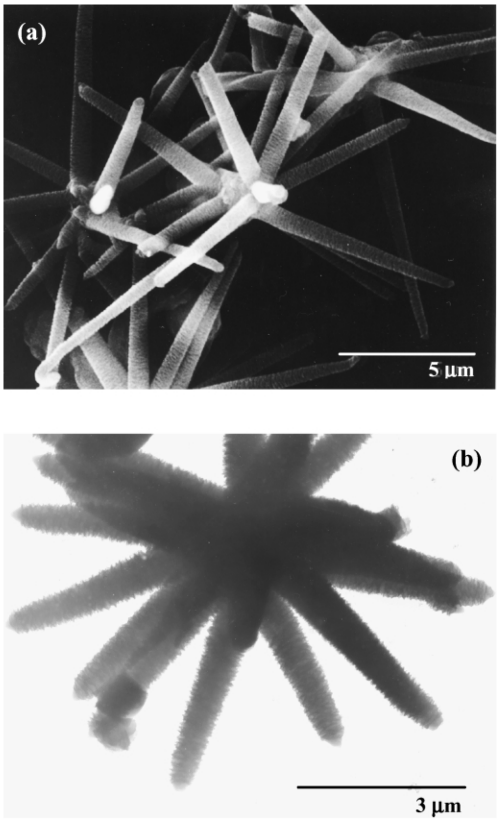

Fig. 1. Scanning electron micrograph (a) and transmission electron micrograph (b) of needle-like crystals.

Fig. 3 shows the WAXS powder profiles of the needle-like crystals. The broad and low-intense halo attributed to the amorphous region is hardly observed. The crystals

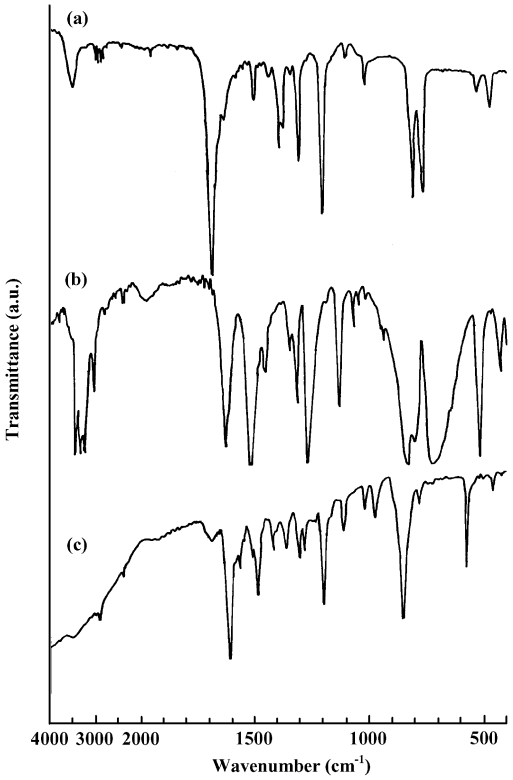

Fig. 2. IR spectra of (a) PPDA, (b) TPA and (c) needle-like crystals.

possess extremely high crystallinity. The sharp Bragg-type reflection peaks are observed at 2θ of 15.3, 20.3, 23.5, 28.9, 39.8 and 43.9°. Crystalline structure of PAZM prepared from PPDA and TPA has not determined accurately so far. Only one model for the crystalline structure had been proposed on the basis of X-ray diffraction and computer modeling [23]. According to this report, the crystalline structure is described by a monoclinic unit cell with the following parameters: $a = 7.42$, $b = 5.39$, $c = 6.11$ Å, $b =$ 94°. However, the fiber identity period estimated from the electron diffraction pattern is 12.69 Å as discussed next, which is twice longer than the proposed c parameter. Although the further investigation is necessary to determine the crystalline structure, we think that c of 12.69 Å is more adaptable than 6.11 Å. The peaks in Fig. 3 can be identified by these parameters as shown in the figure. Fig. 4 shows the transmission electron micrograph and the diffraction pattern of the needle-like crystal. The diffraction pattern is different from the true fiber pattern with cylindrical symmetry, and it consists of the sharp diffraction spots. The spots on the meridian are diffuse, and this may be accounted for by the smaller crystalline area or the axial shifted structure found in aromatic rigid-rod polymers [20]. The observed fiber identity periods is 12.69 Å, which is slightly shorter than 12.95 Å corresponding to the one repeating unit calculated from the data of benzylideneaniline assuming the *trans*-zigzag conformation [21]. This indicates that the meridian of the pattern corresponds to the long axis of the needle-like crystal, and the extended polymer chains align along the long axes of the needle-like crystals. It is very interesting that many lines are clearly observed perpendicular to the long axis of the crystal on its surface. The shish structure of the shish kebab crystal cannot be found in this needle-like crystal. These lines were shown in the incipient POB whiskers prepared for 1 min, and they are the trace of the piling up structure of the lamellae [13,14]. Furthermore, the tip angle of the crystals is ca. 60°. These morphological features strongly suggest that these needle-like crystals are formed through the spiral growth of the oligomer lamellae caused by the screw dislocation as well as the POB whiskers. With respect to the POB whiskers, these lines disappear with time because of the topochemical solid-state polymerization between the lamellae, and the whiskers prepared for 6 h have very smooth surface. PAZM cone-shaped crystals prepared by the self-polycondensation of 4-aminobenzaldehyde for 5 h also had very smooth surface as previously reported [19]. In the case of the needle-like PAZM crystals, due to the condensation reaction of PPDA and TPA the precipitated oligomers have not always one amino group and one formyl group, and some of them have

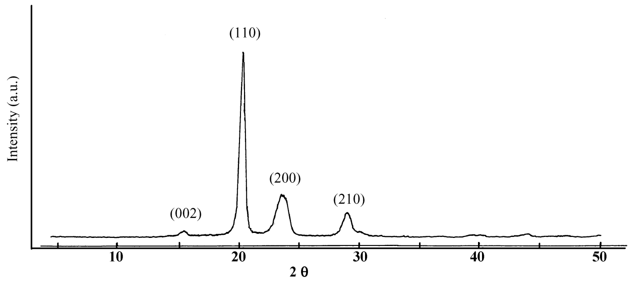

Fig. 3. WAXS powder pattern of needle-like crystals.

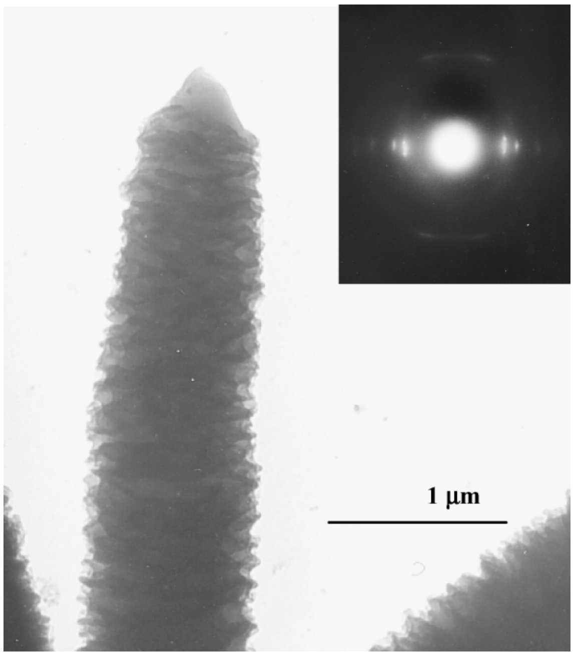

Fig. 4. Enlarged transmission electron micrograph and diffraction pattern of the needle-like crystal.

the same end-groups. The same unreactable end-groups between the oligomers terminate the further polymerization in the crystals, and the trace of the spiral growth is left even after 6 h. Another reason not to disappear the trace of the spiral growth can be thought that the low polymerization temperature of 180 °C is not enough high for solid-state polymerization due to the lack of the oligomer mobility.

Thermal stability of these crystals was measured on TGA in nitrogen atmosphere. It had been reported that the PAZM prepared from PPDA and TPA with conventional azeotropic solution polycondensation showed 2.4 wt% loss at 200 °C, 5.4 wt% loss at 300 °C and 7.2 wt% loss at 400 °C [22]. In contrast to this, the needle-like crystals obtained here exhibit 0 wt% loss at 300 °C, 1.9 wt% loss at 400 °C, and 5 wt% loss temperature of the needle-like crystals is 446 °C. The needle-like PAZM crystals possess the better thermal stability than the PAZM prepared by a conventional method due to the high crystallinity. However, 5 wt% loss temperature of the PAZM cone-shaped crystals prepared by the self-polycondensation of 4-aminobenzaldehyde was 510 °C [19]. The needle-like PAZM crystal is less stable compared with the cone-shaped PAZM crystals prepared from 4-aminobenzaldehyde due to the low molecular weight brought about by a lack of further polymerization in the crystal. This crystal exhibits only the reversible transition at 366.4 °C on a heating scan of DSC. ΔH of this transition is 0.16 kcal mol^{-1}. This crystal dose not show the melting point under the thermal decomposition temperature, and it may be a first order solid–solid transition like POB crystals. This needle-like crystal is in the highest class of thermally stable polymers.

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