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Morphological studies on single crystals and nanofibers of poly(heptamethylene terephthalate)

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Abstract Poly(heptamethylene terephthalate) (poly(7GT)) was synthesized, and its lamellar single-crystals were grown isothermally at 70 °C from a dilute solution in 1-octanol. Poly(7GT) nanofibers were prepared via electrospinning of its solution in 1,1,1,3,3,3-hexafluoro-2-propanol. Morphology of the single crystals and that of as-spun and annealed nanofibers were investigated by transmission electron microscopy. Selected-area electron diffraction (SAED) of the crystals gave a well-defined N-pattern consisting of spot-like *hk*0 reflections, and that of bundles of the annealed nanofibers indicated a highly oriented fiber pattern. From the analysis of SAED diagrams for single crystals and nanofibers, it can be assumed that poly(7GT) takes an orthorhombic crystal system and its unit cell parameters estimated are as follows: $a = 1.409$ nm, $b = 1.480$ nm, c (chain axis) $= 3.392$ nm, and $\alpha = \beta = \gamma = 90°$.

Introduction

Among the engineering plastics, poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT) having excellent physical properties are very popular and utilized world-wide. From the chemical–structural viewpoint, these polymers are classified into the poly(*n*-glycol terephthalate) (poly(*n*GT)) family: *n* is the number of carbon-atoms in the aliphatic component of the polymers. It has been reported that the melting points of poly(*n*GTs) decrease considerably with increasing length of the aliphatic sequence between the aromatic rings in the chain. In addition, a series of poly(*n*GTs) having even numbers of aliphatic carbon-atoms show higher melting temperature than those polymers having odd numbers of aliphatic carbon-atoms[1–3]. The melting temperature is closely related to the crystal structure of poly(*n*GTs). Therefore, many studies have been made to clarify crystal structures of poly(*n*GTs). The crystal structures for those polymers in which *n* is 2, 3, 4, 5, 6, 8, or 10 have been reported so far [4–10]. As for the polymers in which *n* is 7 or 9, however, only the length of *c*-axis in the unit cell has been studied [1].

In order to elucidate the crystal structure of polymer, a fiber diagram which gives the crystal data concerning *c*-axis is necessary. As compared with conventional spinning methods, electrospinning is convenient for the preparation of fiber specimens. However, the thickness of nanofiber is too small and thus the conventional X-ray diffraction measurement is not suitable to the structural analysis of nanofibers.

On the contrary the selected-area electron diffraction (SAED) technique performed by transmission electron microscopy (TEM) is suitable to the analysis of higher

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order structure of nanofibers. Structural investigations on uniaxially oriented thin films of PET [11] or PBT [12] using TEM have shown that both polymers tend to generate a stacked-lamellar structure accompanied with a well-developed fiber diagram. Recently TEM observation has revealed that a well-developed fiber diagram could be obtained from the electrospun nanofibers of poly(heptamethylene terephthalate) (poly(7GT)) and also a stacked-lamellar structure had been constructed in the fibers [13].

In the present article, poly(7GT) was synthesized, and the crystal structure was investigated using TEM by preparing its lamellar single-crystals and by producing nanofibers via the electrospinning.

Experimental procedure

Materials

Poly(7GT) was synthesized by heating heptamethylene glycol with dimethyl terephthalate and butyl titanate as a catalyst in a nitrogen atmosphere for 3 h at a reaction temperature of 180 °C [14]. During the heat treatment, methanol was evaporated. The reaction was completed by heating at a second-stage temperature of 270 °C for 4 h under vacuum. Excess of heptamethylene glycol was evaporated. The synthesized polymer was dissolved in chloroform and settled in methanol. The molecular weight was measured using gel permeation chromatography as $M_w = 38{,}400$ g/mol.

Preparation of lamellar single-crystals

For preparing poly(7GT) lamellar crystals, attempts were made by using several solvents. Then it has been found that 1-octanol can solvate poly(7GT) and complex aggregates have been obtained through isothermal crystallization method. The details are as follows. Poly(7GT) was dissolved in 1-octanol at 180 °C for 10 min and its 0.05 wt% solution was prepared. Then the solution was subjected to the isothermal crystallization at 70 °C for 96 h.

Electrospinning

Poly(7GT) was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and its solution of 5–7 wt% was prepared. Electrospinning was carried out with an "esprayer ES-1000" (Fuence Co., Ltd, Japan). The solution was loaded into a glass syringe having a needle made of stainless steel. The needle was connected to a high-voltage supply. The solution was continuously supplied using a syringe pump at a rate of 20 μL/min through the needle. A voltage of 20 kV was applied for electrospinning. The distance between the needle tip and the collector was ca. 10 cm. Xia and Li [15] demonstrated that electrospun fibers could be aligned in a parallel fashion over long-length scales during the spinning process by using a collector consisting of two conductive strips separated by a void gap of several centimeters. Thus, we designed another new collector consisting of two parallel metal razor blades with their sharp edges pointing upward to the needle, instead of a normal single metal-plate collector [16, 17]. The gap between the blades was ca. 5 mm. The nanofibers on the new collector were annealed at 70 °C for 48 h.

Transmission electron microscopy

Centrifugation and washing with methanol at room temperature were conducted to collect the lamellar crystals. For TEM observation, a drop of lamellar crystals in methanol was deposited onto carbon- or Al-coated grid (namely, onto a carbon support-film or an Al support-film, on a Cu specimen-grid) [18] and allowed to dry. Bundles of annealed nanofibers were mounted on carbon-coated copper grids by directly transferring them from the collector to the grid.

Morphological observations and SAED studies were performed at room temperature using a JEM-200CX (JEOL Ltd, Japan) microscope operated at an accelerating voltage of 200 kV. Images and SAED patterns were recorded on Mitsubishi MEM (Mitsubishi Paper Mills Ltd, Tokyo) or Kodak SO-163 (Kodak Japan Ltd, Tokyo) photographic film.

Results and discussion

Figure 1a shows a TEM image of poly(7GT) lamellar crystals. Aggregation of parallel aligned lath-like crystals has been recognized. Whole appearance of one aggregate is axialite-like. The edges of the crystals are fairly ambiguous. Figure 1b is a SAED diagram for the monolamellar part around the edge of the crystal aggregate. Although the TEM image of poly(7GT) lamellar crystals is ambiguous, a well-resolved and identical SAED diagram has been obtained at every monolamellar part. Figure 2a and b are the enlarged SAED diagram and its schematic representation, respectively. The diagram contains 17 independent reflections. Here we assume the two orthogonal axes, x and y, in the two-dimensional reciprocal lattice, and apply x to a^* and y to b^*. The observed diagram cannot be mirrored in regard to the x-axis nor the y-axis (see Fig. 2b). The lattice parameters, a and b, have been refined with a least-squares method applied to the observed d-spacings of all diffraction spots, and the calculation has given $a = 1.409$ nm, $b = 1.480$ nm, $\gamma = 90°$. From the comparison between the TEM image and the corresponding SAED in Fig. 1, it seems that one of the crystal growth faces is perpendicular to the a^* direction and therefore is plausibly a (100) plane.

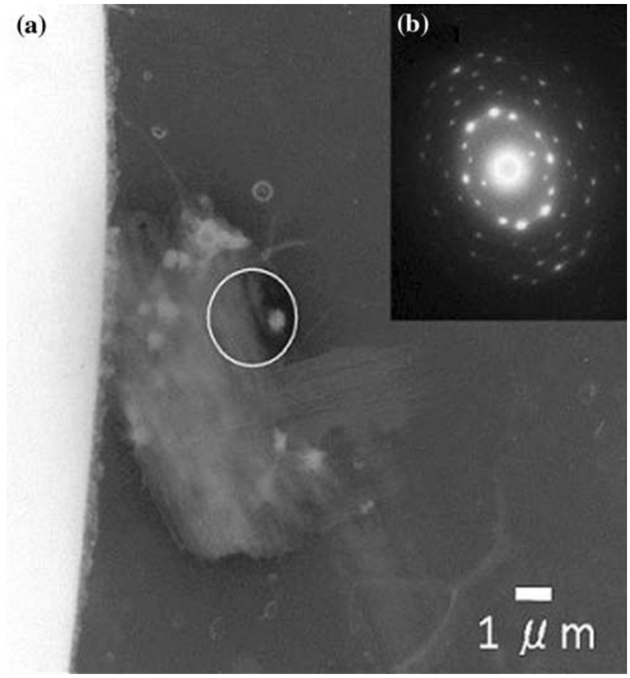

Fig. 1 Morphology (**a**) and the corresponding SAED diagram (**b**) of single crystyals grown isothermally at 70 °C from the solution of 0.5%. Figure 1b is a SAED pattern obtained from one or a few lamellae in the encircled area in (**a**)

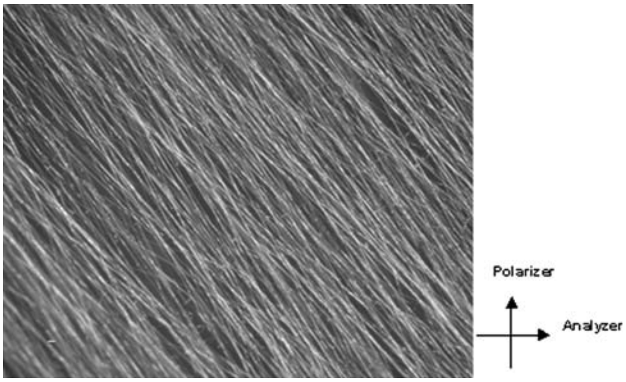

Fig. 3 Polarized light micrograph of as-electrospun nanofibers of poly-7GT aligned using the newly designed collector. The scale bar corresponds to 30 μm

In order to obtain the fiber diagram, poly(7GT) nanofibers have been prepared via the electrospinning method. The nanofibers can be well aligned in a parallel fashion on the newly designed collector which consists of two parallel metal razor-blades. Figure 3 shows a polarized light micrograph of the aligned nanofibers of poly(7GT). It is seen that poly(7GT) molecular chains are oriented parallel to the fiber axis. The TEM images and the SAED diagrams for the as-spun nanofibers and the fibers annealed at 70 °C for 48 h are shown in Figs. 4 and 5, respectively. It is seen that the reflections have become sharper, the intensity of the amorphous halo weaker, as compared to the fibers which had not been annealed. In Fig. 6 the enlarged SAED diagram and its schematic representation for the annealed nanofibers are shown. The diagram contains nine independent reflections. By assuming that the No. 1 spot in Fig. 6b is a reflection from the (008) plane, the observed diagram can be mirrored in regard to the equator and also to the meridian. From the distance between adjacent layer-lines which are shown in Fig. 6b as horizontal straight lines, the lattice parameter *c* (chain axis) has been calculated as 3.392 nm, which is somewhat larger than the previous study [1] by ca. 13%. The observed *d*-spacings and intensities of the reflections in the diffraction diagrams of the poly(7GT) lamellar crystal and nanofiber are summarized in Table 1.

According to the data of other members of the series of poly(*n*GTs), ($n = 2, 3, 4, 5, 6, 8,$ and 10) reported in the previous articles [4–10] all exhibit a triclinic unit cell, in some cases a monoclinic phase. The interpretation of our results should be made referring to the previous data for

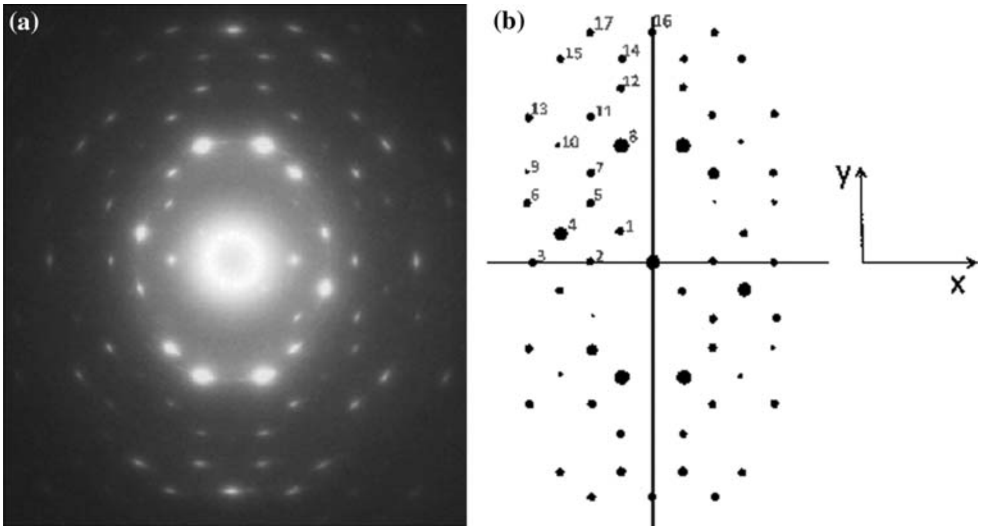

Fig. 2 Enlarged SAED diagram (**a**) and its schematic representation (**b**) from Fig. 1b. x is assumed to be the a^*-axis and y to be the b^*-axis

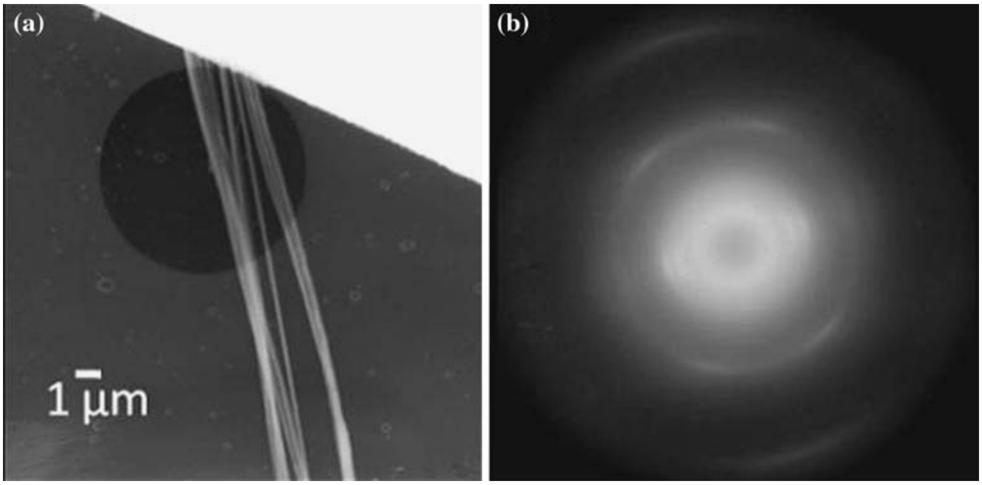

Fig. 4 Morphology (**a**) and the corresponding SAED pattern (**b**) of as-electrospun poly-7GT nanofibers. The SAED pattern (**b**) has been obtained from the encircled area in (**a**)

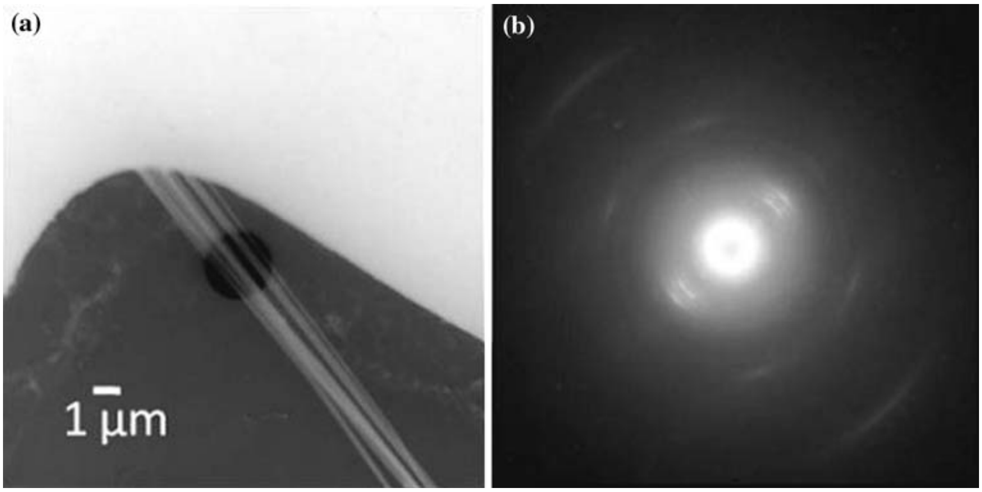

Fig. 5 Morphology (**a**) and the corresponding SAED pattern (**b**) of poly-7GT nanofibers annealed at 70 °C for 48 h. The SAED pattern (**b**) has been obtained from the encircled area in (**a**)

poly(*n*GTs). More precise data concerning the *c*-axis of poly(7GT) will be obtained by tilting the specimen to the incident electron beam. However, the damage to the polymer specimen by the radiation of electron beam should be taken into account at TEM observation. In this study TEM observations have been performed at room temperature, thus all the observation procedures should be completed within 1 min or so to get the diffraction diagram before the decomposition of crystallites. Therefore, X-ray study without damage to polymer is preferable to determine the crystal structure of poly(7GT) more precisely although the development of melt-spinning technique for the production of fully oriented yarns is inevitable.

Recently the authors have confirmed another possible crystal system for poly(7GT) when the melt-crystallization procedure is conducted. The data analyzed for this crystal system will be reported in future. However, it can be concluded at least that poly(7GT) can assume two crystal systems and one of them is an orthorhombic crystal system with the unit cell parameters of $a = 1.409$ nm, $b = 1.480$ nm, c (chain axis) $= 3.392$ nm, $\alpha = \beta = \gamma = 90°$.

Conclusion

Morphological studies on single crystals and nanofibers of poly(7GT) by TEM have revealed that one of the crystal system for poly(7GT) is orthorhombic and its unit cell parameters are as follows: $a = 1.409$ nm, $b = 1.480$ nm, c (chain axis) $= 3.392$ nm, $\alpha = \beta = \gamma = 90°$.

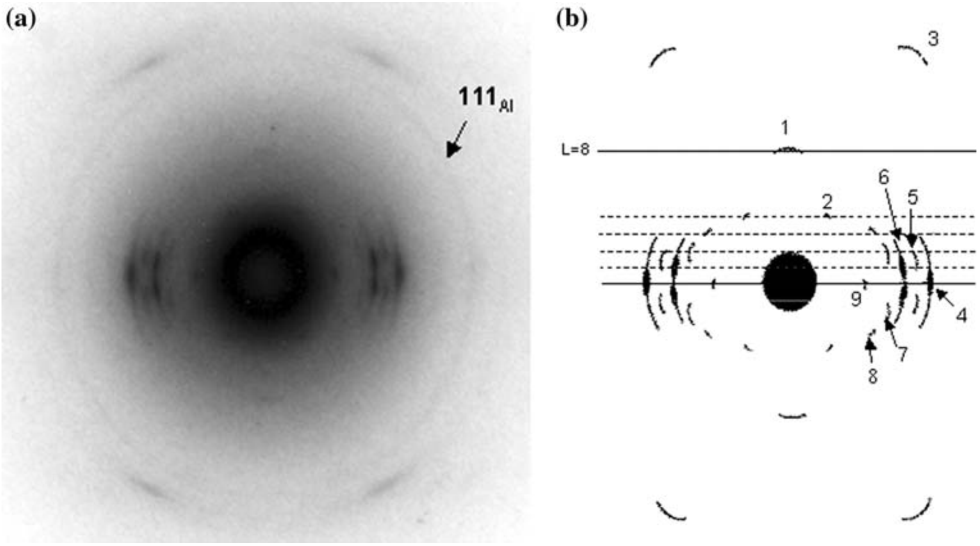

Fig. 6 Enlarged SAED diagram (**a**) and its schematic representation (**b**) from Fig. 5b. Fiber axis is vertical

Table 1 Observed and calculated *d*-spacings from SAED pattern of lamellar crystal

Index[a]	*d*-spacing nm			Intensity	
hkl	Calcd.	Lamella	Nanofiber	Lamella	Nanofiber
110	1.020	1.014		vw	
200	0.705	0.701	0.691	m	m
220	0.510	0.504		w	
310	0.448	0.448		s	
400	0.352	0.352		w	
230	0.404	0.403		m	
420	0.318	0.317		w	
430	0.287	0.287		vw	
140	0.358	0.360	0.364	vs	vs
340	0.291	0.290		vw	
250	0.273	0.275		m	
450	0.227	0.229		w	
620	0.224	0.245		m	
170	0.209	0.207		w	
370	0.193	0.191		w	
080	0.185	0.184		s	
280	0.179	0.159		w	
311	0.444		0.446		s
321	0.394		0.399		m
222	0.489		0.506		w
123	0.567		0.546		vw
014	0.736		0.731		m
008	0.424		0.424		w

vs very strong, *s* strong, *m* medium, *w* weak, *vw* very weak

[a] Indexed in terms of the unit cell with parameters: $a = 1.409$ nm, $b = 1.480$ nm, c (fiber axis) $= 3.392$ nm, $\alpha = \beta = \gamma = 90°$

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