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Stacked-lamellar structure of electrospun poly(heptamethylene terephthalate) nanofibers

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Abstract Poly(heptamethylene terephthalate) (poly(7GT)), which is an aromatic polyesters was synthesized, and nanofibers of poly(7GT) were prepared *via* electrospinning from its solution in 1,1,1,3,3,3-hexafluoro-2-propanol. Uniaxially oriented thin films were also prepared by applying shear strain to molten poly(7GT). Morphology of as-spun and annealed nanofibers and that of uniaxially oriented thin films were investigated by transmission electron microscopy. Selected-area electron diffraction (SAED) of bundles of the annealed nanofibers gave a highly oriented fiber pattern. In addition, dark-field images of the poly(7GT) nanofibers, which had been annealed at 85 °C for 48 h, were taken by using some of the reflections on/near the equator. The images showed a stacked-lamellar structure, in which crystalline lamellae appearing as bright striations oriented perpendicularly to the fiber axis were stacked in the direction of the fiber axis, and the corresponding average long period was estimated at about 19 nm. As for the uniaxially oriented thin films, SAED also gave an oriented fiber pattern. When the annealing of the films was performed similar to nanofibers, crystallization occurred and a stacked-lamellar structure was constructed parallel to the shearing direction. The corresponding average long period was estimated at about 27 nm. By comparing the fiber patterns between annealed nanofibers and thin films, it seems that electrospinning is more effective than uniaxial stretching in enhancing the molecular orientation in the case of poly(7GT).

Introduction

Among 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 widely. These polymers consist of aliphatic and aromatic components in their main chains. 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.

Structural investigations using transmission electron microscopy (TEM) of poly(nGTs) with shorter aliphatic components have shown that, e.g., PET and PBT tend to generate a stacked-lamellar structure [1]. A similar stacked-lamellar structure was recognized for poly(ethylene 2,6-naphthalene dicarboxylate) [2] and also aliphatic biodegradable polyesters on the base of polydioxanone [3]. Moreover, in the case of PBT, a shish-kebab structure was confirmed microscopically and by crystallographic consideration [4].

On the contrary, as for poly(heptamethylene terephthalate) poly(7GT), only the length of c-axis parameter in the unit cell has been determined [5]. Morphological studies have not been reported so far.

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In the present paper, nanofibers and uniaxially oriented thin films of poly(7GT) were, respectively, prepared via the electrospinning of the solution and by applying shear strain to the melt, respectively, and then the resulting morphologies were studied by TEM.

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 [6]. 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 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 Mw = 38,400 g/mol.

Electrospinning

Poly(7GT) was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and its solution of 5%–7% 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 [7] 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 [3, 8]. The gap between the blades was ca. 5 mm. The nanofibers on the new collector were annealed at 70 or 85 °C for 48 h.

Preparation of uniaxially oriented thin films

A 0.5 wt% solution of poly(7GT) in HFIP was dropped and spread on a glass slide that was preheated to 180 °C. The amorphous cast film was covered with another glass slide and the system was kept at this temperature for 10 min. Then, the thin molten polymer film was sheared by displacing one of the two glass slides and then quenched to room temperature [2, 4]. Annealing of the film was carried out at a temperature of 85 °C for 48 h.

Transmission electron microscopy

For TEM observation, bundles of annealed nanofibers were mounted on carbon-coated copper grids by directly transferring them from the collector to the grid. The oriented thin film was mounted directly on a grid by using an aqueous solution (ca. 25%) of polyacrylic acid [9].

Morphological observations and selected-area electron diffraction (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 1 shows the SEM images of nanofibers as-spun from (a) 5, (b) 7 wt% solutions of poly(7GT) deposited on

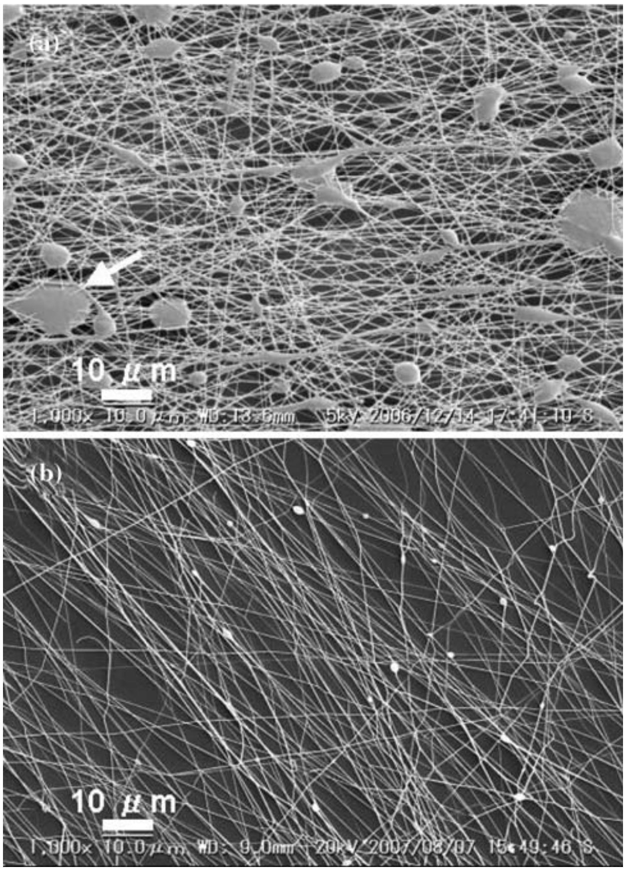


Fig. 1 SEM images of electrospun nanofibers deposited on a flat collector. Concentrations of poly(7GT) solution are **a** 5 wt% and **b** 7 wt%

a flat collector. The number of beads generated generally increased with decreasing concentration of the spinning solution. Therefore, the electrospinning in this study was performed using a solution of 7 wt%, where only very few beads have been observed. Figure 2a shows a bright-field TEM image of as-spun nanofibers of poly(7GT) prepared using the collector consisting of two conductive strips. It is seen that the fibers are aligned almost parallel to each other. A well-developed fiber pattern is observed in the corresponding SAED diagram in Fig. 2b, which shows that the poly(7GT) molecules are highly oriented along the fiber axis.

Figure 3 shows a TEM micrograph and a corresponding SAED pattern of nanofibers annealed at 70 °C for 48 h. The aspect of fibers is unchanged after the annealing (see Fig. 3a). However, the reflections have become sharper, and the intensity of the amorphous halo weaker, as compared to the fibers that had not been annealed (see Fig. 2). It is seen that crystallization has proceeded keeping the orientation of poly(7GT) molecular chains. The increase in crystallinity is probably due to thickening and/or crystal perfecting for primary lamellae.

Dark-field imaging of poly(7GT) nanofibers annealed at 85 °C for 48 h using some of the reflections on/near the equator is shown in Fig. 4. Many bright striations are observed, which run in the direction perpendicular to the fiber axis. The width of these striations is in the range of 17–34 nm. They appear to be part of a stacked-lamellar structure oriented in the direction of fiber axis. The thickness of the lamellae amounts to ca. 11 nm, and the average long period is estimated to ca. 19 nm, as indicated in Fig. 4.

Figure 5a shows a bright-field TEM image of an as-sheared thin film of poly(7GT) and Fig. 5b is the corresponding SAED diagram where a well-developed fiber pattern is observed similar to the case of nanofibers (see Fig. 2b). It is confirmed that poly(7GT) molecules are highly uniaxially oriented in the shearing direction.

Figure 6 shows a TEM micrograph and a corresponding SAED pattern of uniaxially oriented thin films annealed at

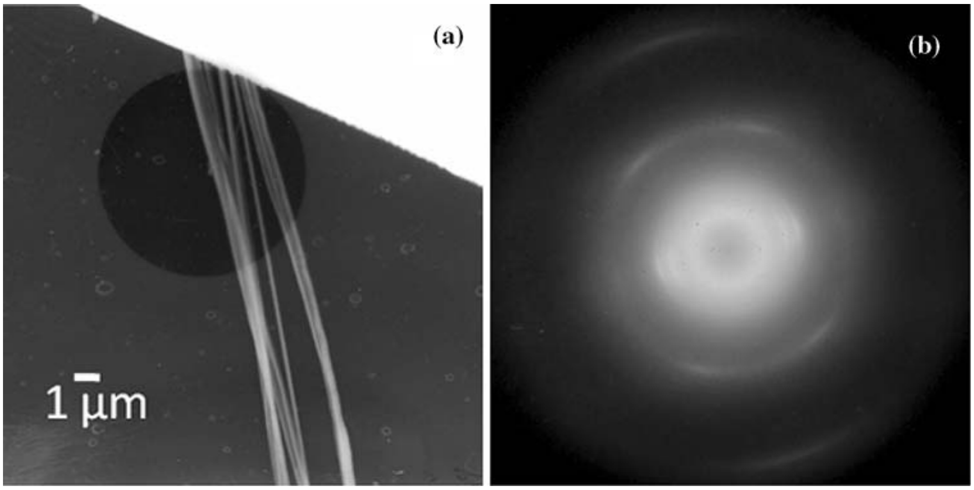


Fig. 2 Morphology (**a**) and the corresponding SAED pattern (**b**) of as-spun poly(7GT) nanofibers. The SAED pattern **b** was obtained from the encircled area in **a**

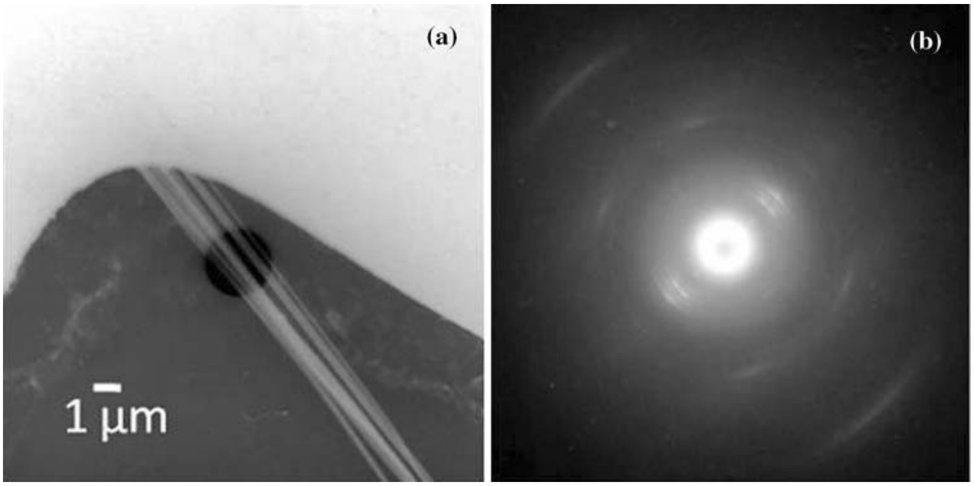


Fig. 3 Morphology (**a**) and the corresponding SAED pattern (**b**) of poly(7GT) nanofibers annealed at 70 °C for 48 h. The SAED pattern **b** was obtained from the encircled area in **a**

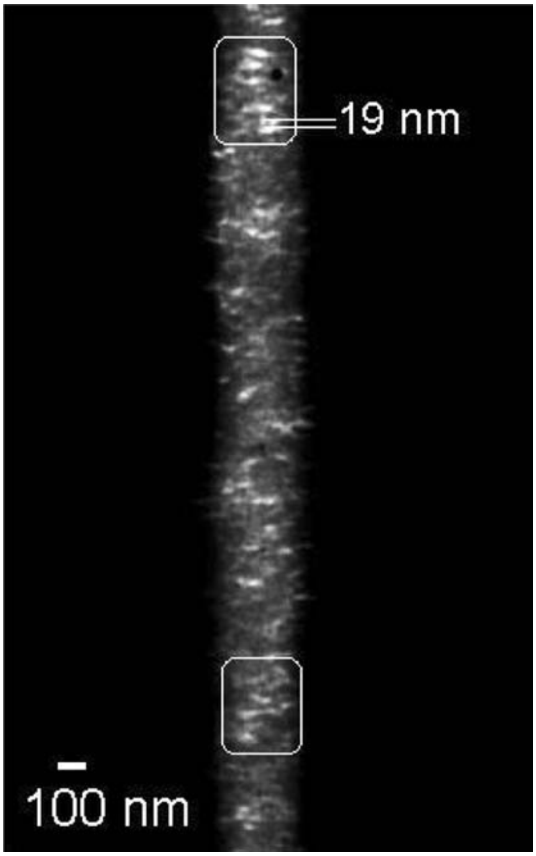


Fig. 4 Dark-field TEM image of the electrospun poly(7GT) nanofiber annealed at 85 °C for 48 h. This image was taken by using some of the reflections on/near the equator in the SAED diagram. Fiber axis is vertical. Typical stacked-lamellar structures can be seen in the squares marked

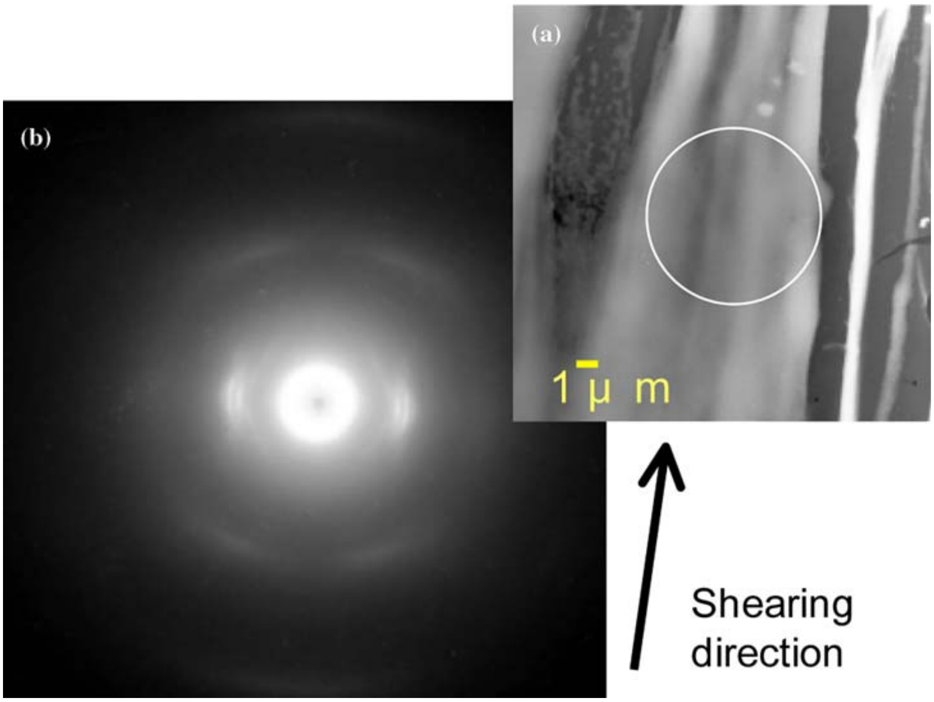
85 °C for 48 h. The surface of the film has been even after the annealing. The reflections have become sharper, and the intensity of the amorphous halo weaker, as compared to the films that had not been annealed (see Fig. 5). It is seen that crystallization has proceeded keeping the orientation of poly(7GT) molecular chains. The increase in crystallinity is probably due to thickening and/or crystal perfecting for primary lamellae.

Dark-field imaging of poly(7GT) uniaxially oriented thin films annealed at 85 °C for 48 h using some of the reflections on/near the equator is shown in Fig. 7. Many bright striations are observed, which run in the direction perpendicular to the shearing direction similar to the case of nanofibers (see Fig. 4). In this case, however, the width of these striations is in the range of 31–63 nm, the thickness of lamellae amounts to ca. 13 nm, and the average long period is estimated as ca. 27 nm, as indicated in Fig. 7.

When the fiber patterns were compared between nanofibers and thin films obtained from poly(7GT) after annealing, sharper diffraction spots were obtained for nanofibers, which suggests that electrospinning is more effective in enhanceing the molecular orientation in the case of poly(7GT).

As for PET, the lamellar thickness as well as the long period are greatly influenced by the deformation speed of molten polymer. In the high speed spinning process, by increasing the spinning speed from 5 to 9 km/min, the thickness of lamellae for as-spun fibers increased from 7 to 9 nm; on the contrary, the long period decreased from 24 to 12 nm [10]. The thickness of lamellae for poly(7GT) in this

Fig. 5 Morphology (**a**) and the corresponding SAED pattern (**b**) of as-sheared poly(7GT) thin film. The SAED pattern **b** was obtained from the encircled area in **a**



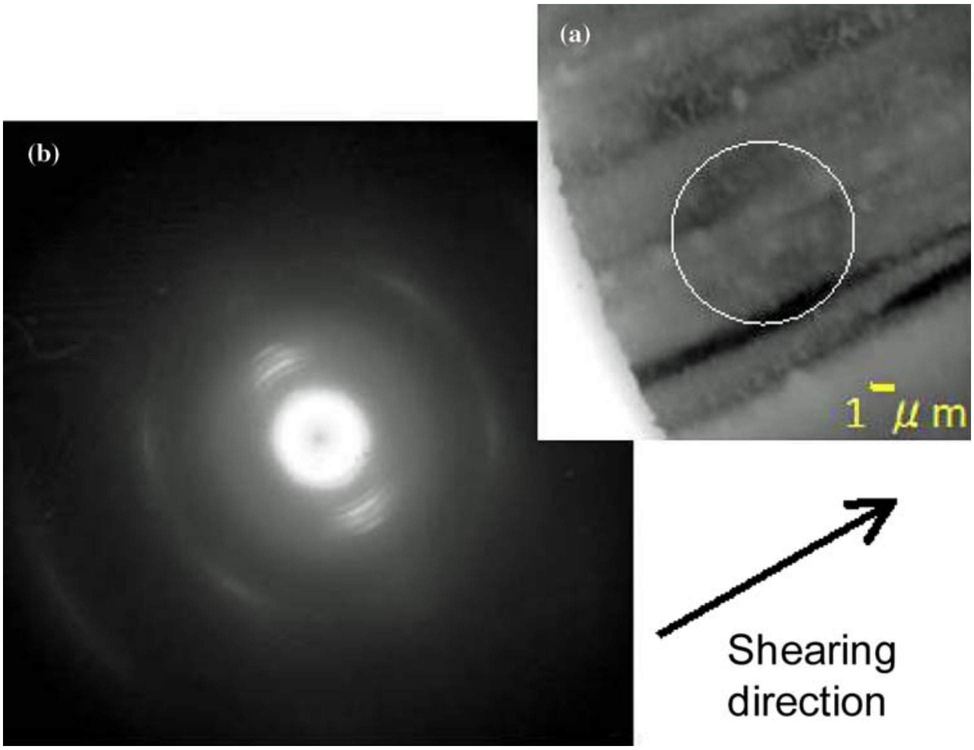


Fig. 6 Morphology (**a**) and the corresponding SAED pattern (**b**) of poly(7GT) uniaxially oriented thin film annealed at 85 °C for 48 h. The SAED pattern **b** was obtained from the encircled area in **a**

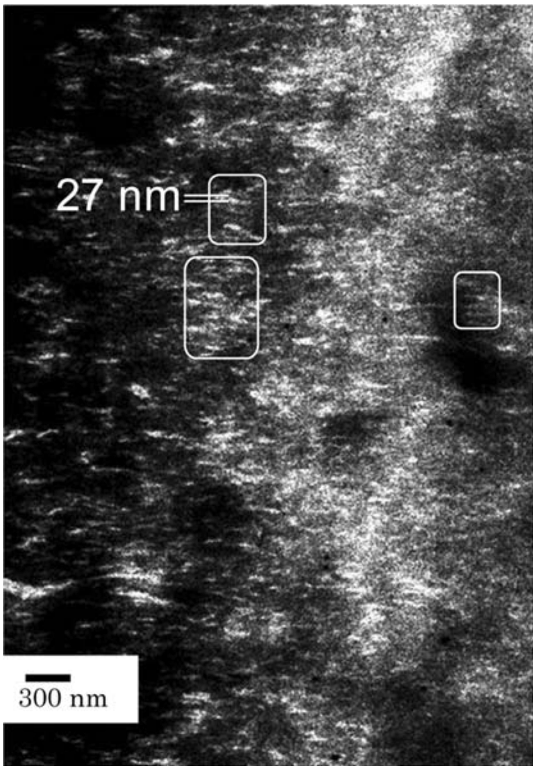


Fig. 7 Dark-field TEM image of the uniaxially oriented thin film of poly(7GT) annealed at 85 °C for 48 h. This image was taken by using some of the reflections on/near the equator in the SAED diagram. Shearing direction is vertical. Typical stacked-lamellar structures can be seen in the squares marked

study is almost comparable to the value of PET although the long period is fairly larger. In the case of PET, the decrease in the long period is of great relevance to the increase in crystallinity. Although very long term annealing treatments had been performed on the poly(7GT) nanofibers and films, the long periods have become almost double as compared with that of PET. The formation of large amorphous domains is probably due to the long aliphatic chains in poly(7GT) that tend to form loose loop foldings between the primary lamellae.

In order to elucidate the physical properties of poly(7GT), a fundamental study on the crystal structure of this polymer is necessary. Recently the authors have reported that poly(7GT) seems to take an orthorhombic crystal system and its unit cell parameters are as follows: $a = 1.409$ nm, $b = 1.480$ nm, c (chain axis) $= 3.392$ nm, $\alpha = \beta = \gamma = 90°$[11]. However, the data of other members of the series of poly(nGT) ($n = 3, 4, 5, 6, 8, 10$) reported in the literature all exhibit a triclinic unit cell, and in some cases, a monoclinic phase [12–20]. Further investigations are needed to discuss the relevance of our work on poly(7GT) to those for other members.

Conclusion

Morphological studies on nanofibers and uniaxially oriented thin films of poly(7GT) revealed that poly(7GT) also tends to develop a stacked-lamellar structure similar to in the case of PET and PBT, both of which have shorter aliphatic components than poly(7GT). The structural parameters for the lamellae were influenced by the processing method. Electrospinning seems to be more effective than uniaxial stretching in enhancing the molecular orientation.

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