

# Polymer Nanofibers Prepared by Template Melt Extrusion

Huayi Li,<sup>1,2</sup> Yucai Ke,<sup>1</sup> Youliang Hu<sup>1</sup>

<sup>1</sup>Joint Laboratory of Polymer Science and Materials, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

<sup>2</sup>Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China

Received 28 June 2004; accepted 19 February 2005

Published online in Wiley InterScience (www.interscience.wiley.com).

DOI 10.1002/app.22597

**ABSTRACT:** Combining the template method with the extrusion technology, polymer nanofibers have been prepared when molten polymer is forced through the pores of anodic aluminum membrane and cooled to complete the nanofiber formation process. The microstructures of nanofibers are determined by SEM, TEM, XRD, and DSC. The results suggest that the PE nanofibers consist of extended-

chain crystals and the transition from an orthorhombic to a hexagonal phase and the latter phase melting occurs at 159.8°C. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1018–1023, 2006

**Key words:** template melt extrusion, polymer nanofibers, polyethylene, polystyrene

## INTRODUCTION

Extrusion technology is used broadly in thermoplastic process. The molten polymer is forced by extruder screw through a mold or spinning die in the head of extrusion devices, and then cooled in air or cooling fluid whereby it solidifies to complete the continued tube, rod, plate, and fiber formation process.

Anodic aluminum oxide membranes (AAOMs) having straight and separated cylindrical pores with monodisperse diameters in nanometer scale have been used as templates to prepare nanoscopic rods<sup>1–5</sup> and tubes,<sup>6,7</sup> which have attracted considerable attention from both the scientific studies and their potential utilization. These nano-products illustrated in above papers, however, were based upon the template-wetting technique. That is, the AAOMs were placed on top (or bottom) of the molten or solution polymer, and with the help of wetting, capillary force, or gravity, these polymer melts or solutions could enter the pores of the membrane; then the nanorods (or nanofibers) or nanotubes with length equal to or less than the thickness of AAOM can be obtained after the molten polymers were cooled or the solution polymers were evaporated to remove the solvents or submerged in a coagulation bath to precipitate. But the viscosity of molten polymer is too high to enter the pores completely, and so the length of nano-product is usually

much shorter than that of the pore of AAOM. Polyethylene (PE) nanofibers were also prepared by extrusion polymerization.<sup>8</sup> Metallocene catalysts were supported on the walls of the pores of mesoporous silica fibers, the ethylene was introduced and polymerized in the pores, and PE nanofibers were synthesized. In the present study, we prepared long polymer nanofibers by combining the extrusion technology and template method. AAOM as a mold is fixed in a simple extrusion appliance we designed and constructed, polymer melts are pressed into the pores of the AAOM, and the polymer nanofibers are preserved when AAOM is removed. We term this method “template melt extrusion.”

## EXPERIMENTAL

### Materials

PE was prepared by the catalyst 2,6-diacetylpyridinebis(2,6-diisopropylanil)FeCl<sub>2</sub>, which was synthesized according to the literature.<sup>9</sup> The polymerization condition was MAO (Al)/Fe = 4900, in 50 mL of toluene, under 1 atm of ethylene at 25°C for 25 min. The molecular weight of the PE polymer prepared was  $M_n = 1.5 \times 10^3$ ,  $M_w/M_n = 44.8$ . Polypropylene (PP,  $M_n = 1.0 \times 10^5$ ,  $M_w/M_n = 4.4$ ), polystyrene (PS,  $M_n = 8.5 \times 10^4$ ,  $M_w/M_n = 2.7$ ), and polyethylene terephthalate (PET; intrinsic viscosity, 0.65 dL/g) were provided by Yanshan Petrochemical Co. Ltd. AAOM were purchased from Whatman International Ltd.

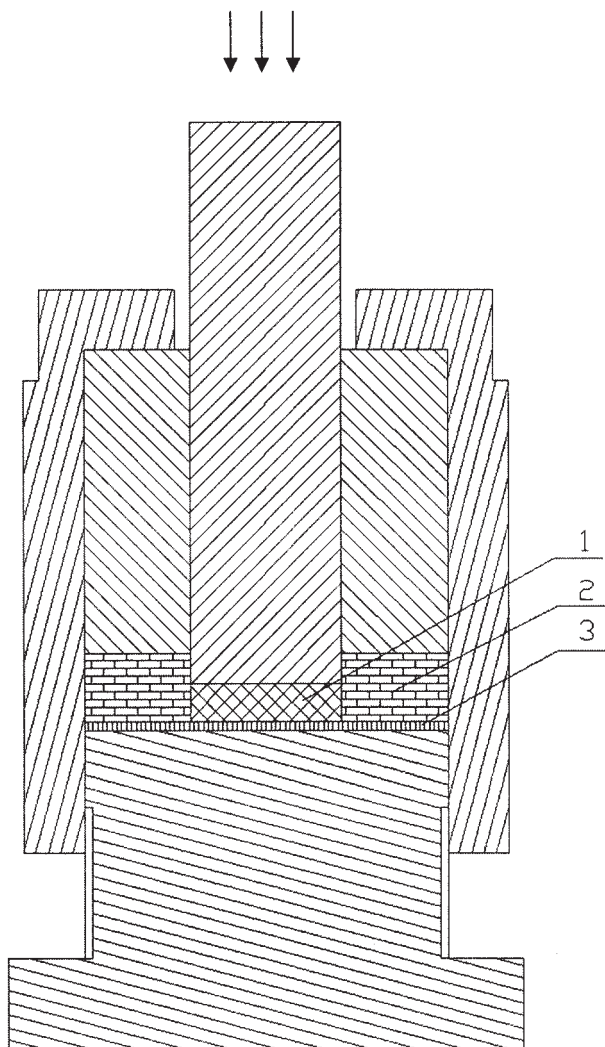
### Extrusion appliance

The template melt extrusion method can be easily carried out. But an appliance is necessary not only to

Correspondence to: Y. Hu (huyl@iccas.ac.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20334030.

Contract grant sponsor: SINOPEC.



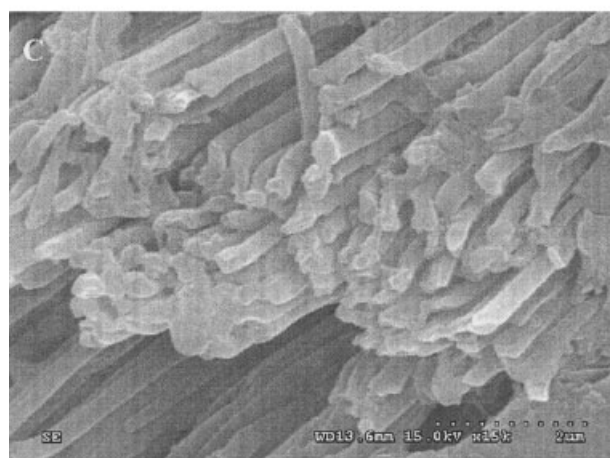
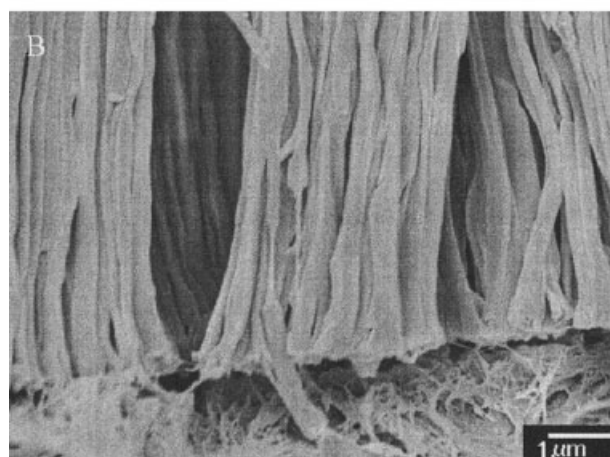
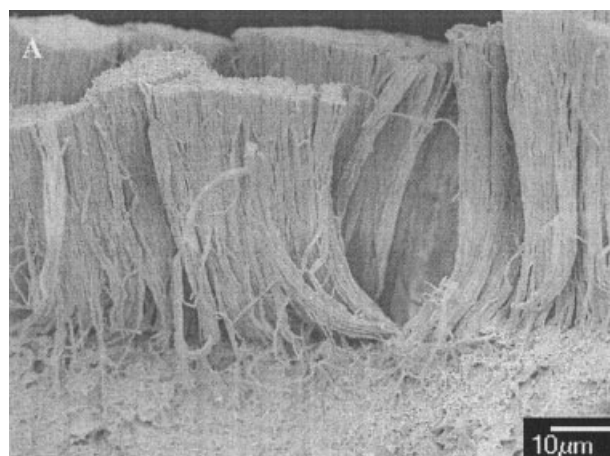
**Figure 1** The appliances for template melt extrusion process. (1) Feeding polymer. (2) PTEF seal. (3) Alumina membrane.

support the aluminum membranes (because the membranes are too thin and crisp to bear the pressure) but also to restrict the movement of molten polymer along the direction of the pores of AAOM. Figure 1 shows the cross-sections of the appliance we designed and illustrates how it works. The material of the appliance is stainless steel. Part 1 is feeding polymer, part 2 is polytetrafluoroethylene (PTEF) seal, and part 3 is aluminum membrane.

### Preparation of nanofibers

The appliance was assembled with parts (1), (2), and (3) as shown in Figure 1, and then placed on the hot plate of a compressor with heat- and temperature-controlled functions; and then the polymer melt was forced as indicated by the arrows in Figure 1. The temperature of the hot plane varied with different

polymers, such as PE at 190°C, PS at 200°C, PP at 230°C, and PET at 300°C. The pressure was 0.5 MPa. Two hours later, the hot plane was stopped heating but



**Figure 2** FESEM images of polymer nanofibers. (A) PE nanofibers "grow" on the surface of PE bulk feeding film; (B) PE nanofibers are not uniform in diameter. (C) The ends of aligned PS nanofibers display clear-cut circular shape in the main region and in some places they show a thin film.

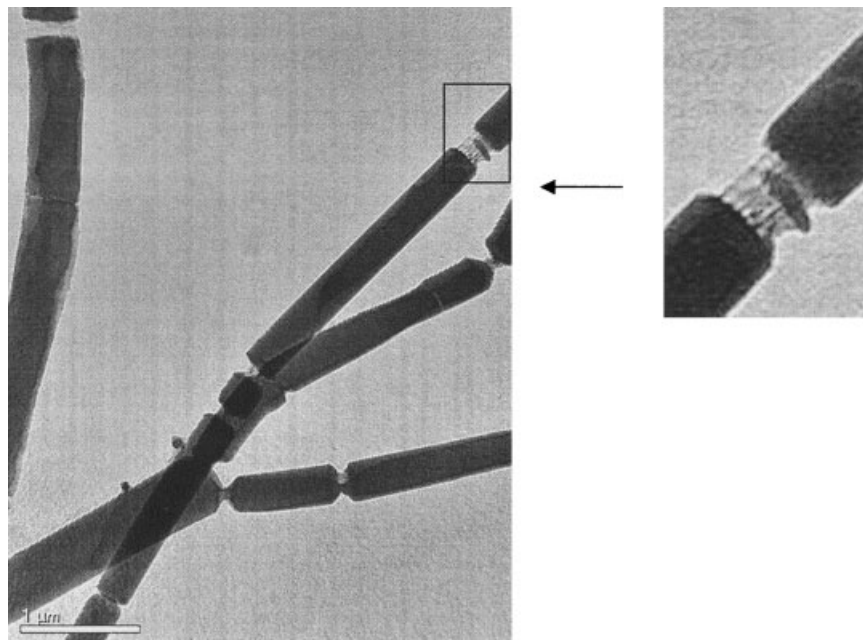


Figure 3 TEM photograph of PS nanofibers.

the pressure was maintained till the system slowly cooled to room temperature. After disassembling the equipment, the polymer/aluminum membrane composite was easily taken off.

### Characterization

Field emission scanning electron microscopy (FESEM) was performed using JEOL JSM 6700F at 3.0 kV. The samples were coated with a thin layer of gold prior to FESEM observation. Transmission electron microscopy (TEM) was performed by JEOL J1020 instrument with 200 kV accelerating voltage. The X-ray Diffraction (XRD) was performed using Regaku D/max-2500, Cu radiation (40 kV, 200 mA). The melting temperatures ( $T_m$ ) of the polymer and its nanofibers were measured by differential scanning calorimeter (DSC; PE DSC-7), circularly heating from 40°C to a presetting temperature at 10°C/min.

## RESULTS AND DISCUSSION

We prepared PE, PP, PS, and PET nanofibers via the aforementioned method; thus, this simple template melt extrusion process is a general method for the preparation of nanofibers composed of thermoplastics. Here, we focus only on the results of PE nanofibers. Figure 2 shows the FESEM images of ordered PE and PS nanofiber arrays attached to the bulk feeding film after the alumina substrate has been removed. It can be seen in Figure 2(A) that the PE nanofibers “grow” on the surface of the bulk feeding polymer film and the nanofibers do not conglutinate to poly-

mer bulk, indicating that the AAOM is not fractured in the processing. The length of the fibers is similar to that of the pores of AAOM (60  $\mu\text{m}$ ). Under high magnification [Fig. 2(B)], it can be found that the PE fibers are not uniform in diameter (ranging from 150 to 400 nm, the specified diameter of AAOM pores is 200 nm); even each nanofiber is not uniform in diameter. The ends of aligned PS nanofibers [as shown in Fig. 2(C)] display clear-cut circular shape in the main region, but in some places they show a thin film (denoted as a thin glued film) because the PS melts passing beyond the pores of AAOM agglutinate with each other. In fact, the thin glued films existed in the process of the preparation of all polymer nanofibers, which indicate that the polymer melt enters the pore of the AAOM mainly via external pressure but not capillary force. Figure 3 shows the TEM images of PS nanofibers. It is very interesting that some places show the crazes of the PS nanofibers before being broken down. The craze must have been caused by ultrasonic or other manipulation, but not by processing, because the craze was not found in Figure 2(C), which was recorded before ultrasonic.

To obtain the isolated nanofibers without any supporting film, three steps have been carried out. Figure 4 illustrates this processing. The thin glued film must be removed first. We used the method of solvent etching. The polymer/aluminum membrane composite was immersed in solvent for 0.5–2 min, the thin glued film was dissolved, and the fibers were seldom affected. The PE film can be etched by orthodichlorobenzene at 135°C and the PS film can be done by tetrahydrofuran at room temperature. After removal

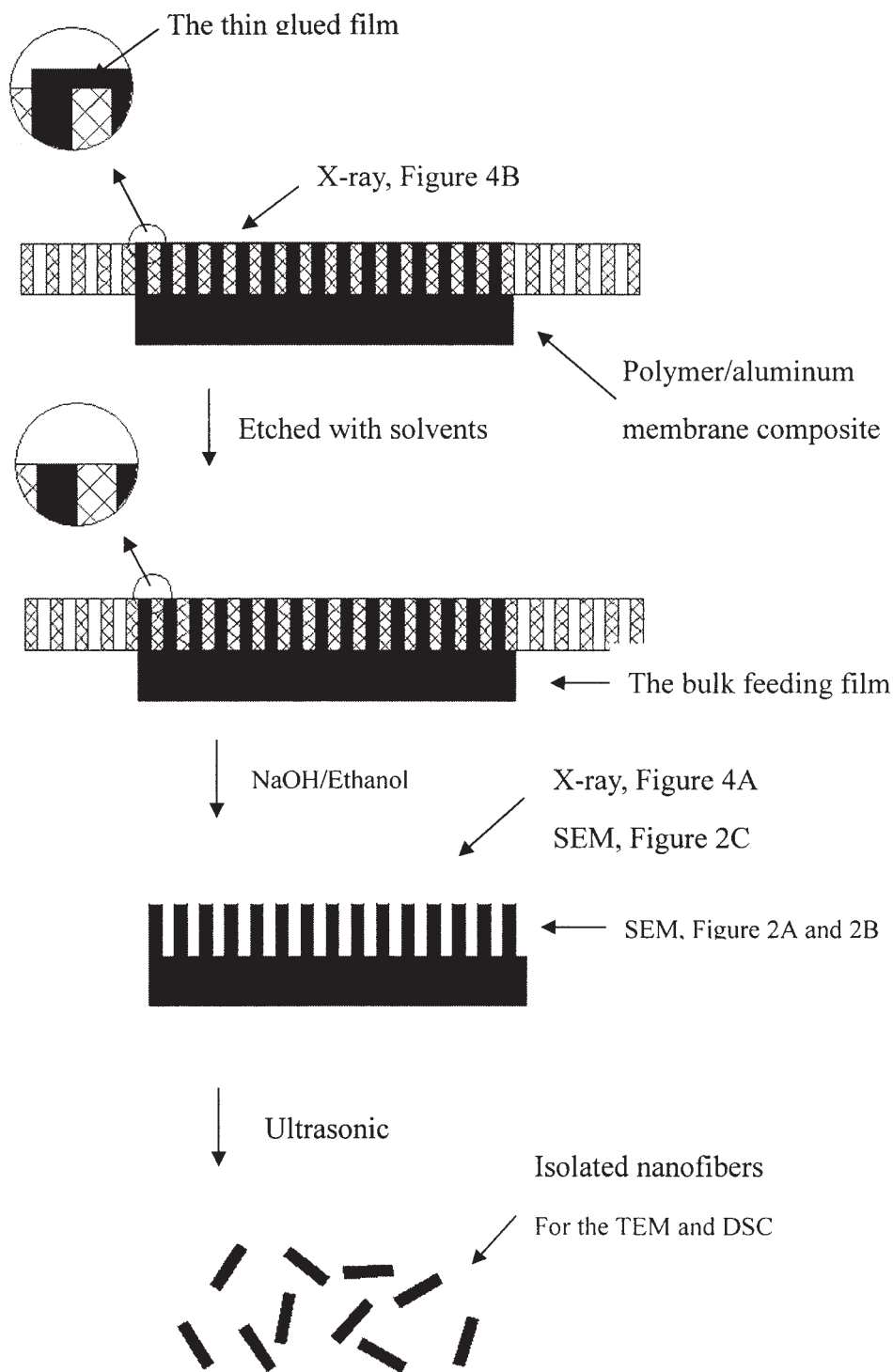


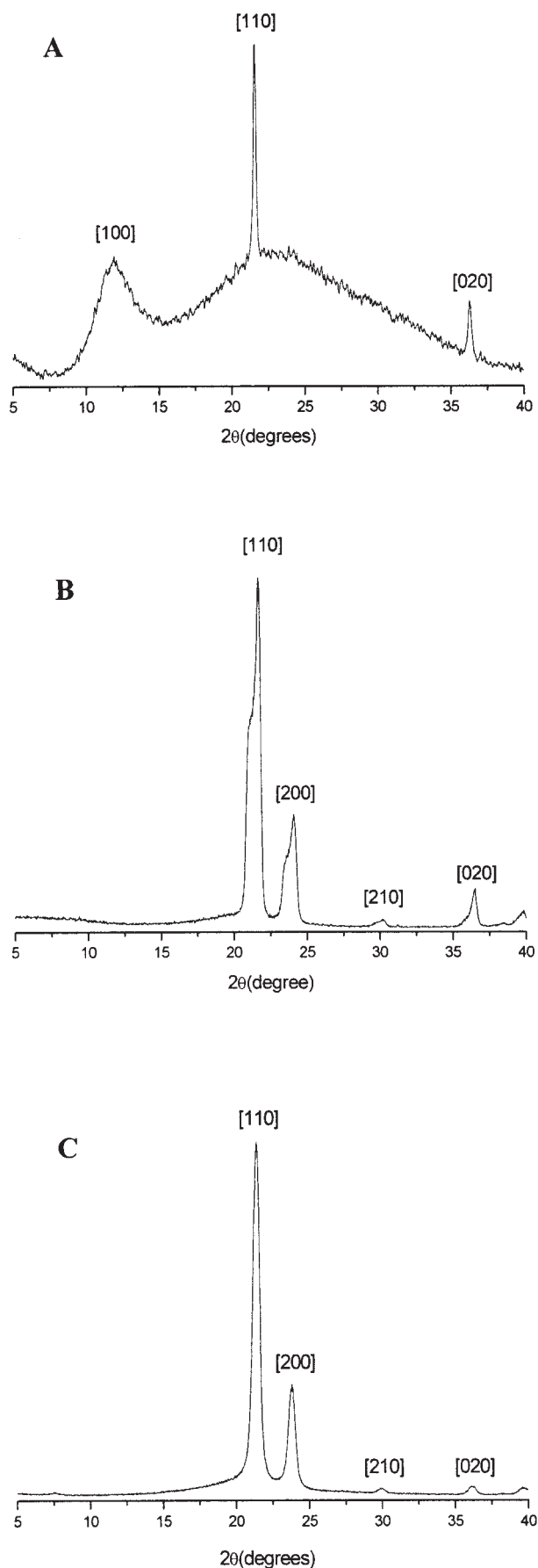
Figure 4 Scheme for preparing isolated nanofibers.

of the AAOM with 20% (by weight) NaOH/Ethanol, nanofiber arrays on the bulk feeding film can be reserved. At last, the nanofibers can be broken down from the bulk feeding film by ultrasonic (in ethanol for 5 min) to form isolated ones.

The XRD patterns of PE nanofibers, the thin glued film, and the powder obtained from polymerization

are represented in Figure 5. It can be seen that PE raw powder has typical four diffraction peaks of [110], [200], [210], and [020] planes, which appeared at 21.6°, 23.8°, 30.2°, and 36.3°, respectively,<sup>10</sup> and is a typical orthorhombic crystal. The thin glued film has similar peaks (Fig. 5(B)) to those of the PE powders; only the shapes of [110] and [200] are slightly different.

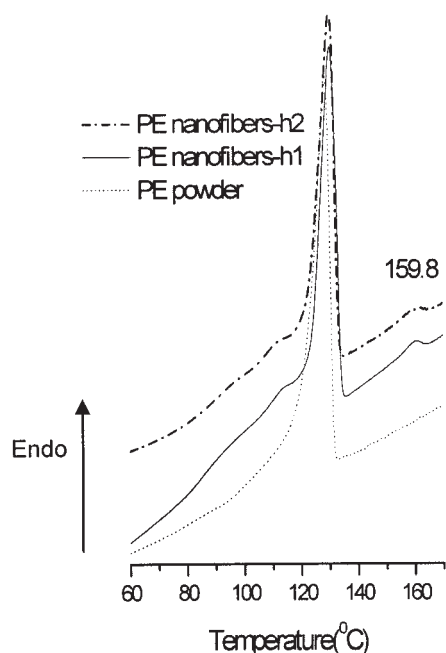




The XRD pattern of aligned PE nanofiber arrays (Fig. 5(A)) displays three peaks [100], [110], and [020] at  $11.9^\circ$ ,  $21.6^\circ$ , and  $36.3^\circ$ , respectively. It is surprising, however, that the peaks of [200] and [210] disappeared, and the diffraction of [100] with a broad peak centered at  $11.9^\circ$  dramatically appears. This diffraction peak does not appear in the polyethylene stretched 500%<sup>11</sup> or in the polyethylene nanofibers synthesized by extrusion polymerization.<sup>6</sup> Considering the possibility by that the orthorhombic crystals of the nanofibers contain extended chains, the orientation should be along the direction of fiber axes. This is because that the diameters of PE nanofibers in the constrained pores are a little bit higher than the lamellar length of ordinary PE crystals ( $\sim 100$  nm).<sup>12</sup> The PE chains will be sheared or extended by the velocity gradient when the melt is being extruded and are quite likely prevented from folding within the constrained pores of aluminum membrane. Thus the extended-chain crystals are produced by the crystallization when the extruded nanofibers were cooled. In addition, taking into account of the XRD pattern, the diffraction of [100] shows a broad peak centered at  $11.9^\circ$  and extended to  $2\theta$  below  $10^\circ$ , presumably indicating that a small amount of the hexagonal-chain packing crystals existed as the nanofibers within constrained pores of membrane during cooling process.<sup>13</sup> But this consideration must be confirmed in further studies.

Thermal analysis of PE powder and nanofibers is showed in Figure 6. In the first scanning, the nanofibers are heated up to  $170^\circ\text{C}$ ; the endothermic peak of nanofibers that appeared at  $130.7^\circ\text{C}$  is a little higher than that of PE powder at  $129.0^\circ\text{C}$ , while the broad endothermic peak centered at  $159.8^\circ\text{C}$  is not observed in PE powder. In the second scanning, the nanofibers are heated up to  $250^\circ\text{C}$ , the endothermic peak centered at  $159.8^\circ\text{C}$  still exists with a little broad peak. In the third scanning, however, the peak centered at  $159.8^\circ\text{C}$  disappears and the endothermic curve is similar to that of PE powder. The new endothermic peak at high temperature is attributable to the phase transition of the extended-chain crystals from an orthorhombic phase to a hexagonal phase and the melting of the hexagonal phase, as reported in literatures.<sup>8,14,15</sup> The hexagonal crystals can be destroyed when the temperature is above  $250^\circ\text{C}$ , and so in the first and the second scanning, the endothermic peak exists at  $159.8^\circ\text{C}$ , but after the nanofibers are heated to  $250^\circ\text{C}$ , the hexagonal phase is destroyed and this endothermic peak disappears naturally. In addition, the heat of fusion ( $\Delta H_0$ ) of the PE powder is  $219.6$  J/g, but the  $\Delta H_1$  of nanofibers

**Figure 5** XRD pattern of (A) the aligned PE nanofibers arrays, (B) the thin-glued film, and (C) PE powder obtained from polymerization.



**Figure 6** The DSC melting curves of PE powder and the first scanning (h1), the second scanning (h2) of PE nanofibers

in the first scanning is 274.1 J/g, which is actually superheating; and it is also evident that the nanofibers consist of extended-chain crystals. In the second scanning, the  $\Delta H_2$  of PE nanofibers is 230.7 J/g, which is lower than  $\Delta H_1$ , but is higher than  $\Delta H_0$ . Because the temperature in the first scanning is not high enough to convert all extended-chains of the PE nanofibers to folded-chains, the endothermic peak at 159.8°C still exists, and  $\Delta H_2$  is higher than  $\Delta H_0$ . In the third scanning, the  $\Delta H_3$  of PE nanofibers approximately equals  $\Delta H_0$ .

Masuda et al.<sup>16</sup> reported that two-step anodization provided a method for the preparation of high chemical mechanical metal membrane. If the high chemical mechanical metal membrane can be made, we assumed that continued polymer nanofibers could be prepared by this template melt extrusion technique. According to the traditional dry-spinning and wet-spinning techniques, the template extrusion can also be used to prepare the continued polymer nanofibers, in which the polymer is dissolved and the solution is

extruded under pressure through the template spinneret first; then the solution is evaporated to remove the solvent and nanofibers are solidified in the case of dry spinning or is submerged in a coagulation bath and nanofibers are precipitated in the case of wet spinning.

## CONCLUSIONS

Combining the extrusion technology in the polymer industry with the template method in the nanotechnology, we have developed "template melt extrusion" method to prepare polymer nanofibers in the length as the thickness of template. This method can be applied in all thermoplastics. The PE nanofibers prepared by this method have extended-chain crystals as indicated by XRD and DSC. With heat of fusion being close to superheating, the endotherms of the nanofibers exhibit two melting peaks, the one at lower temperature being a little higher than that of the PE raw powder obtained from polymerization, and the one at higher temperature reflects the phase transition of the extended-chain crystals from an orthorhombic phase to a hexagonal phase.

## References

1. Martin, C. R. *Science* 1994, 266, 1961.
2. Moon, S. I.; McCarthy, T. J. *Macromolecules* 2003, 36, 4253.
3. Rahman, S.; Yang, H. *Nano Lett* 2003, 3, 439.
4. Feng, L.; Li, S. H.; Zhai, J. *Synthetic Met* 2003, 135, 817.
5. Feng, L.; Li, S. H.; Li, H.; Zhai, J.; Song, Y.; Jiang, L.; Zhu, D. *Angew Chem Int Ed Engl* 2002, 41, 1221.
6. Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Neilsch, K.; Schilling, J.; Choi, J.; Gosele, U. *Science* 2002, 296, 1997.
7. Ai, S. F.; Lu, G.; He, Q.; Li, J. B. *J Am Chem Soc* 2003, 125, 11140.
8. Kageyama, K.; Tamazawa, J.; Aida, T. *Science* 1999, 285, 2113.
9. Britovsek, G. J. P.; Bruce, M.; Gibson, V. C. et al. *J Am Chem Soc* 1999, 121, 8728.
10. Bunn, C. W. T. *Faraday Soc* 1939, 35, 482.
11. Krimm, S.; Tobolsky, A. V. *J Polym Sci* 1951, 7, 57.
12. Niegisch, W. D.; Swan, P. R. *J Appl Phys* 1960, 31, 1906.
13. Bassett, D. C.; Block, S.; Piermarini, J. *J Appl Phys* 1974, 45, 4146.
14. Pennings, A. J.; Zwijnenburg, A. *J Polym Sci Polym Phys Ed* 1979, 17, 1011.
15. Yasuniwa, M.; Enoshita, R.; Takemura, T. *Jpn J Appl Phys* 1976, 15, 1421.
16. Masuda, H.; Fukuda, K. *Science* 1995, 268, 1466.