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Time-Dependent Transformation of an Electrospun Isotactic Poly(1-butene) Fibrous Membrane

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ABSTRACT: Isotactic poly(1-butene) (i-PB) fibrous membranes with fiber diameters on the order of microns were prepared from polymer solutions using mixed solvents via electrospinning. As demonstrated by FE-SEM, unexpected structures such as curled, twisted ribbon fibers and hollow hemisphere (HHS) on a string appeared depending on the type of solvents used. Furthermore, it was observed that electrospun fibrous membranes and solvent cast films gave rise to different crystalline modifications even though they were formed from the same solutions. This may be due to different crystallization times and stresses induced during the electrospinning process. The electrospun fibrous membrane contained both form I (twinned hexagonal structure) and metastable form II (tetragonal structure) immediately after spinning. The metastable form II gradually transformed into the stable form I at room temperature over the span of several days. This transformation was observed to occur more rapidly with increased temperature. In comparison, solvent cast films contained a mixture of form III (orthorhombic structure) and a small amount of form I′ (untwinned hexagonal structure) and was stable at room temperature. However, form III is the dominant crystal structure in the solvent cast film, as determined by WAXD. These transformations were investigated as a function of aging time by Fourier transform infrared and Raman spectroscopy as well as X-ray diffraction and differential scanning calorimetry.

Introduction

Polyolefins, including polyethylene (PE), polypropylene (PP), poly(1-butene) (PB), and poly(4-methyl-1-pentene) (P4M1P), comprise the largest portion of the commercial polymer industry. Of particular interest is poly(1-butene), which exists in different extents of regioregularity: atactic, isotactic, and syndiotactic. The isotactic form (i-PB), first synthesized by Natta,[1] is a semicrystalline polymer that exhibits four different crystalline structures, depending on the preparation.[2−5] These are summarized in Table 1.

Since Miller and Holland[6] first reported the time-dependent polymorphism in PB under ambient conditions, interest in forms I and II has increased. Form II is metastable and is commonly found when i-PB is crystallized from the melt. Form II transforms slowly and irreversibly into the thermodynamically stable form I at room temperature. Physical and mechanical properties such as density, crystallinity, and tensile strength are affected during this transformation.

The crystalline transformation (II → I) has been shown to be influenced by pressure,[7] temperature,[8] and mechanical deformation,[9,10] and it has been studied extensively using various techniques such as DSC,[11] WAXS,[7,12] and small-angle X-ray scattering (SAXS).[12] Marigo et al.[12] showed that the crystalline transformation kinetics could be monitored by analysis of the form II (200) and the form I (110) reflections in the WAXS and SAXS patterns. In addition, form III is commonly crystallized from solution.[13] Geacintov et al. reported that form III is prepared by casting from various solvents such as benzene, toluene, carbon tetrachloride, ρ-xylene, or decalin.[13] Form III, however, is not only stable at room temperature but also stable under stretching and the application of pressure at room temperature.[13] Furthermore, form I′ can be crystallized from both solution and melt.[14] However, both forms I′ and III depend on the nature of solvent, the concentration, and the crystallization temperature.[13,15]

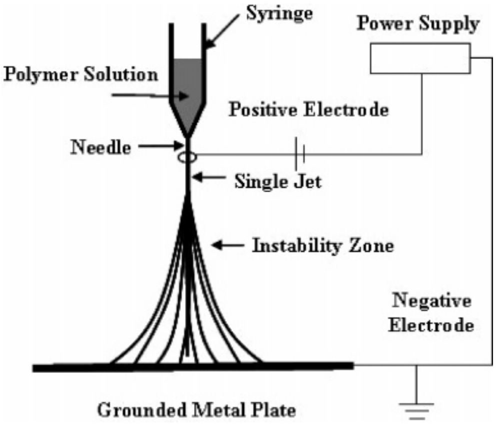

Figure 1. Schematic diagram of the electrospinning setup.

Electrospinning is an effective method for the preparation of micron to nanometer diameter fibers from solution or from the melt.[16−18] A number of polymers have been successfully processed using this technique, but polyolefins, which are only slightly soluble in most solvents at room temperature, have not been electrospun until recently.[19,20]

In this paper, we report on the time-dependent crystalline phase transformations in PB fibrous membranes electrospun from a mixed solvent system as a function of aging at room

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Table 1. Crystallographic Data for Isotactic Poly(1-butene)

form	crystal lattice	helix	unit cell dimension (Å) *a*	*b*	*c*	T_m(°C)
I	hexagonal (twinned)	3/1	17.7	17.7	6.5	120−135
I′	hexagonal (untwinned)	3/1	17.7	17.7	6.5	90−100
II	tetragonal	11/3	14.6	14.6	21.2	110−120
III	orthorhombic	4/1	12.5	8.9	7.6	90−100

temperature in comparison with a similarly electrospun heat treated fibrous membrane and a solvent cast film. The behavior of all samples was investigated by FT-IR and Raman spectroscopy as well as WAXD and DSC.

Experimental Section

Materials. Isotactic poly(1-butene) (i-PB) was purchased from Aldrich. The molecular weight distribution was found to be very broad with a weight-average molecular weight of 556 000 and a number-average molecular weight of 93 000 by gel permeation chromatography (GPC). The i-PB was dissolved in a mixture of cyclohexane, acetone, and dimethylformamide (DMF) (80/10/10 by weight ratio) at 60 °C at a weight concentration of 2% and then cooled to 25 °C for electrospinning. All chemicals were used without further purification. Films were obtained by solvent casting from the same solution used for electrospinning.

Electrospinning. Figure 1 shows a diagram of the electrospinning setup employed in this work. The polymer solution was poured into a 3 mL syringe equipped with a 21 gauge needle (Hamilton). A high-voltage power supply (Gassman High Voltage) was used to generate a potential difference of 11 kV between the needle and an aluminum foil-covered grounded metallic plate placed 15 cm from the tip of the needle.

Characterization. The morphology of the electrospun fibrous membranes was characterized using a field emission scanning electron microscope (FE-SEM, JSM-7400F, JEOL) operating at 2 kV and 10 μA. To monitor the changes in the transformation during aging, a Nexus 670 spectrometer (Thermo Nicolet) was used. The spectra were recorded from 750 to 4000 cm^{-1} at a resolution of 4 cm^{-1} and an average of 128 scans were coadded, while Raman spectra were acquired with a Kaiser Holospec spectrograph (Kaiser Optical Systems, Inc., East Hanover, NJ) using a 785 nm diode laser for excitation. X-ray diffraction patterns were measured with a Rigaku Dmax 2500 diffractometer operating at 30 kV and 150 mA using Cu Kα radiation with a wavelength of 0.154 05 nm as the X-ray source. Scans were recorded over a 2θ range of 5°−30°. Thermal properties were evaluated under a N_2 atmosphere using a differential scanning calorimeter (DSC, Q100, TA Instruments). The heating rate in all experiments was 20 °C/min. Additional hyper-DSC experiments were carried out using a Diamond DSC (Perkin-Elmer) with a cryogenic cooling accessory under a helium purge.

Results and Discussion

An example of the morphology of the electrospun fibrous membrane prepared under the conditions described above (2 wt % in a 80/10/10, cyclohexane/acetone/DMF dissolved in at 60 °C, spun at 25 °C) is shown in Figure 2A,B. Interestingly, unexpected features such as curled and twisted ribbon-shaped fibers with irregular twist points were observed. This most likely results from the use of a combination of solvent and nonsolvent in the mixed solvent system. These effects have been explained as arising from a rapid evaporation of solvent from the outer portion of the fiber followed by slow diffusion and evaporation of solvent from the inside of the fiber with a subsequent collapse of the fiber into a ribbonlike structure.[21] "Twists" originate when two collapsed regions form ribbons that are perpendicular when they meet. Also, the hollow hemisphere on a string morphology was observed when using mixed solvents of cyclohexane and DMF (80/20, w/w) (Figure 2C). Similar structures have previously been reported for polystyrene (PS).[22] However, the size of the hemispheres of i-PB (under 10 μm) was found to be much smaller than that of PS (20−30 μm).

The infrared bands for the polymorphous crystalline forms I and II and the transformation of form II into form I were reported by Luongo and Salovey,[23,24] and the vibrational modes for i-PB have been assigned.[25−27] Shown in Figure 3 are the FTIR spectra of an electrospun fibrous membrane, a film formed by solvent casting, and an electrospun fibrous membrane that was heated at 80 °C for 1 h after electrospinning, obtained as a function of aging time over the span of 3 weeks at room temperature.

There are distinct differences among these samples in the 950−800 cm^{-1} range, specifically among four characteristic bands. The band at 925 cm^{-1} (CH_2 and CH_3 rocking) is known to be characteristic of form I while 905 cm^{-1} (CH_2 and CH_3 rocking) is characteristic of form II and III.[23,24,28] Also, the bands

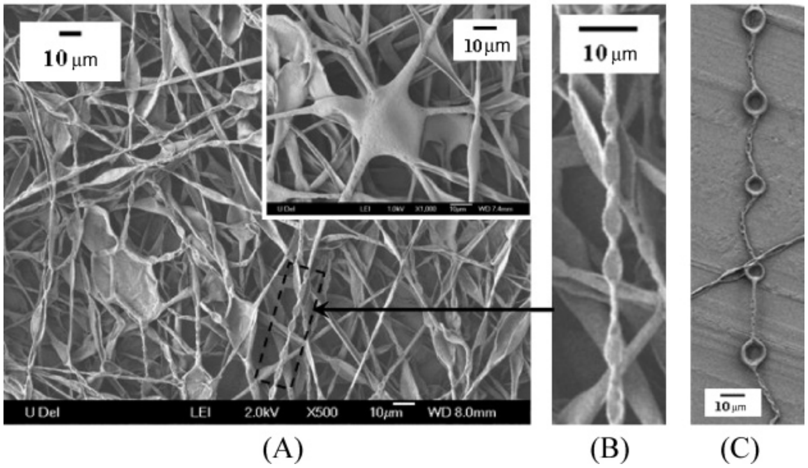


Figure 2. FE-SEM images of electrospun i-PB fibrous membrane from solutions in (A, B) cyclohexane/acetone/DMF (80/10/10, w/w/w) and (C) cyclohexane/DMF (80/20, w/w).

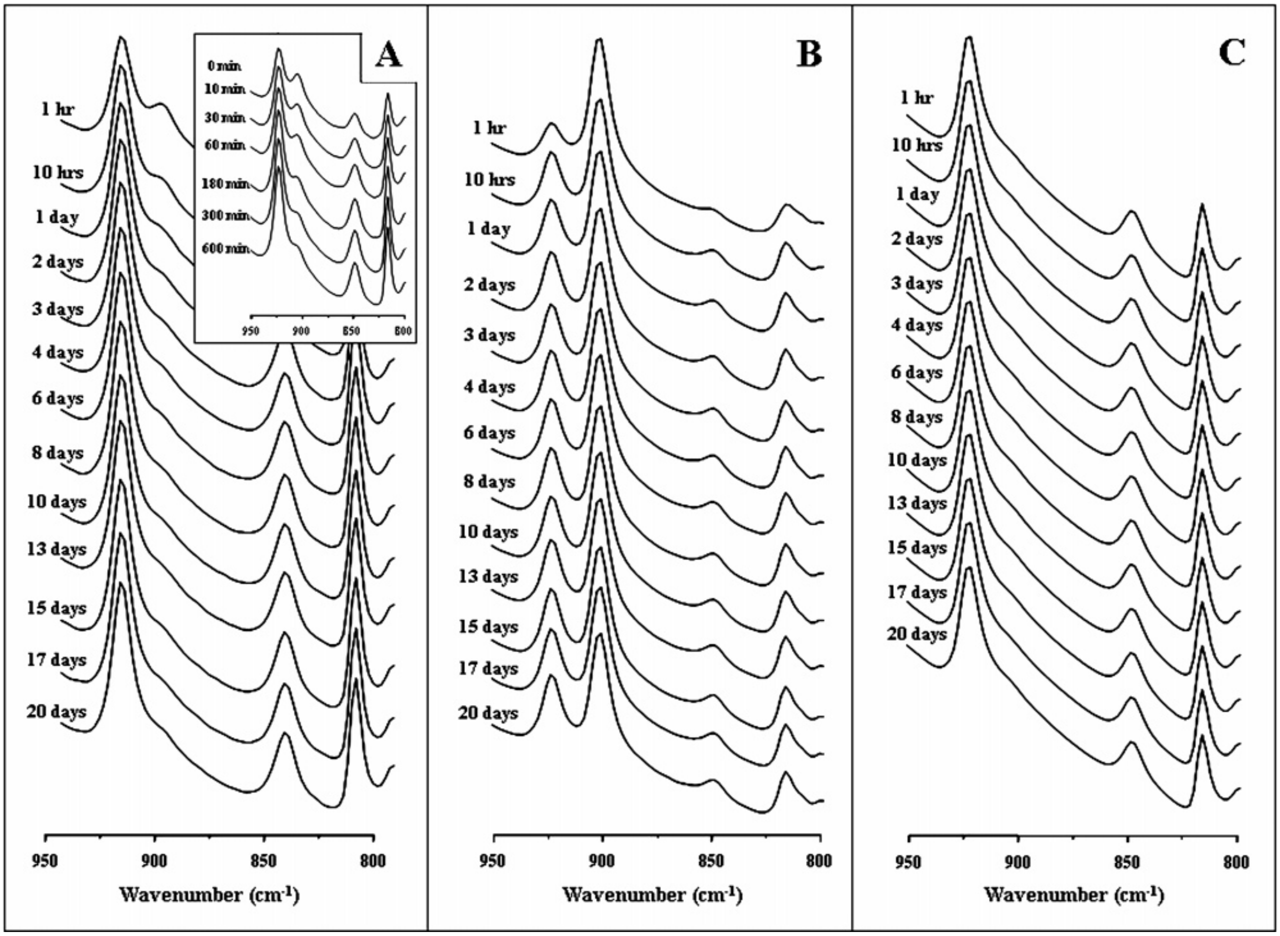


Figure 3. FT-IR spectra of (A) the electrospun fibrous membrane, (B) the solvent cast film, and (C) the electrospun fibrous membrane heat treated at 80 °C for 1 h as a function of the aging time at room temperature.

at 845 cm^{-1} (CH_2 and CH_3 rocking and CC symmetric vibration) and 815 cm^{-1} (CH_2 rocking) can be used to monitor the transformation between forms.[23] In the FT-IR spectra, these corresponding absorption bands are observed at 924, 904, 849, and 816 cm^{-1}, respectively.

For the electrospun fibrous membrane, the bands at 924, 849, and 816 cm^{-1} become stronger during aging, but the band at 904 cm^{-1} gradually diminishes and disappears after about 2 days at room temperature. After an aging time of 2 days, all these bands are no longer dependent on the aging time (Figure 4). These results indicate that a mixture of crystalline forms I and II coexists when the fibers were spun, and form I is the dominant crystalline structure. However, a portion of the form II fraction is transformed into the thermodynamically more favorable form I during aging at room temperature. The band at 904 cm^{-1} was not observed in the spectrum of the electrospun fibrous membrane heat treated at 80 °C for 1 h (Figure 3C), further supporting the hypothesis that the form II present immediately after electrospinning was metastable and converted to form I at 80 °C. The FTIR spectrum of the electrospun fibrous membrane aged for several days at room temperature is very similar to the electrospun fibrous membrane heat treated at 80 °C for 1 h. This result indicates that form I content of the electrospun fibrous membrane can be accelerated by heat treatment at elevated temperatures.

In the solvent cast film, four bands at 924, 900, 849, and 816 cm^{-1} (Figure 3B) are observed in the FT-IR spectrum. Among them, the intense band at 900 cm^{-1} is characteristic of form III. Bands at 849 and 816 cm^{-1} are also observed in form III, but the intensity has not changed during aging. In addition, the band at 924 cm^{-1} can be assigned as a band of form I′.

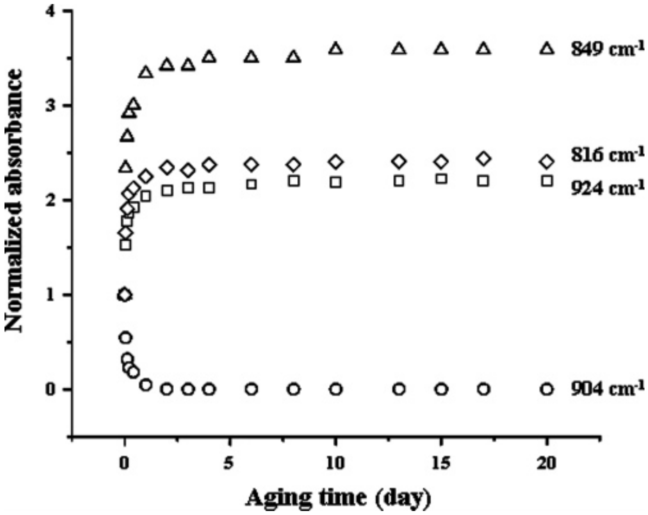


Figure 4. Change of absorbance intensity of the 924 cm^{-1} (form I), 904 cm^{-1} (form II), and 849 and 816 cm^{-1} bands in the electrospun fibrous membrane with aging time.

All bands observed in both the electrospun fibrous membrane (heat treated at 80 °C for 1 h; form I) and the solvent cast film (form III) are not time dependent. Hence, this indicates that form I and III are stable crystalline structures at room temperature.

After aging 20 days at room temperature the crystalline structure of all samples is also evident in the Raman spectra,

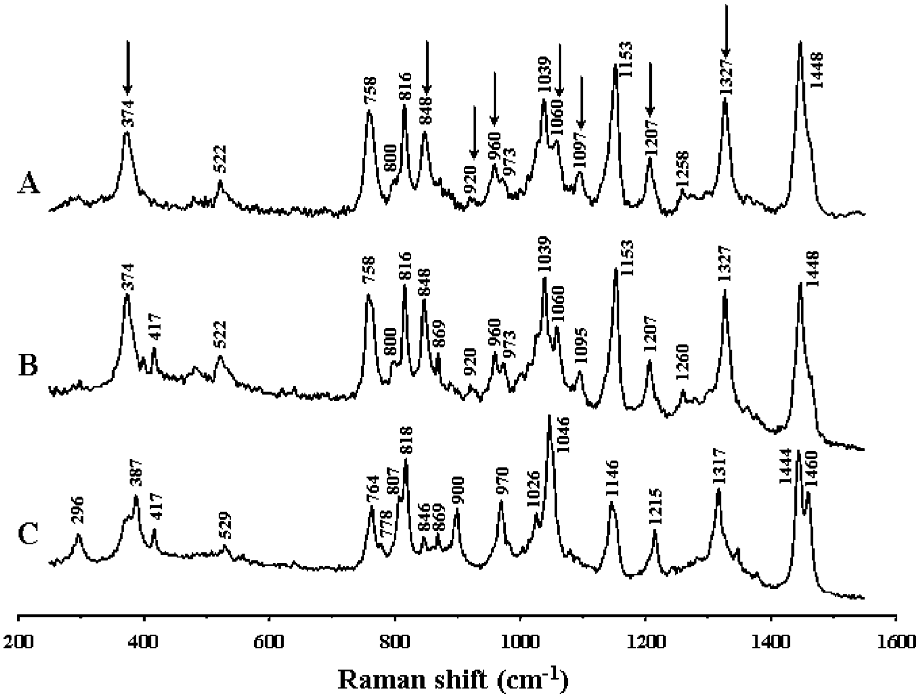


Figure 5. Raman spectra of (A) the electrospun fibrous membrane, (B) the electrospun heat treated fibrous membrane, and (C) the solvent cast film after 20 days aging time at room temperature. The arrows indicate bands characteristic of form I.

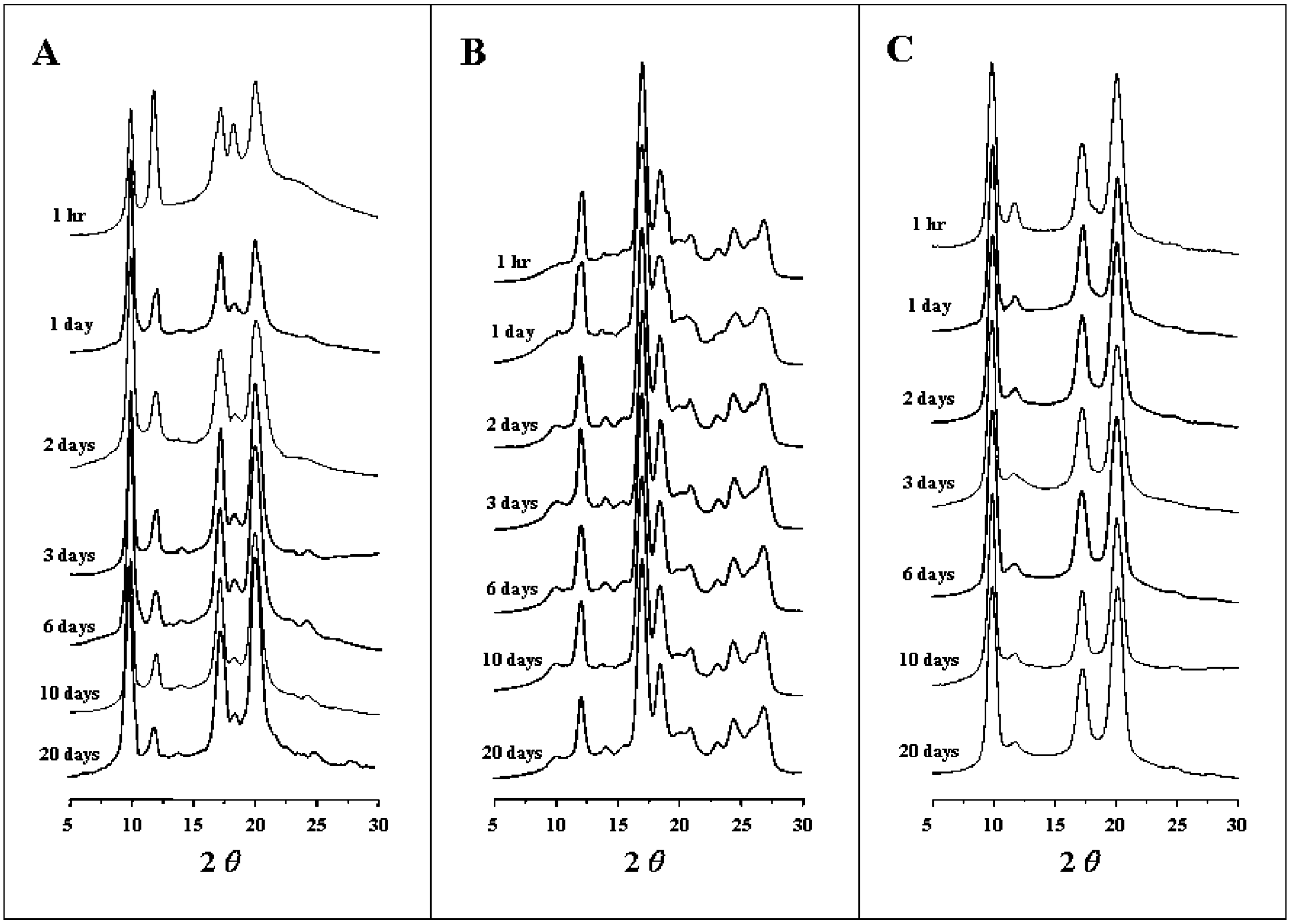


Figure 6. WAXD profiles of (A) the electrospun fibrous membrane, (B) the solvent cast film, and (C) the electrospun heat treated fibrous membrane with aging time.

as shown in Figure 5. The Raman spectra of electrospun fibrous membrane and the electrospun fibrous membrane heat treated at 80 °C for 1 h clearly demonstrate the existence of form I, having characteristic bands at 374 (CCC bending), 848 (CH_3 rocking), 920 (CH_3 rocking and CH_2 twisting), 960 (CH_3 rocking and CC stretching), 1060 (CC stretching), 1097 (CC stretching), 1207 (CH_2 twisting), and 1327 cm^{-1} (CH_2 wagging). On the other hand, the Raman spectrum of the solvent cast film is quite

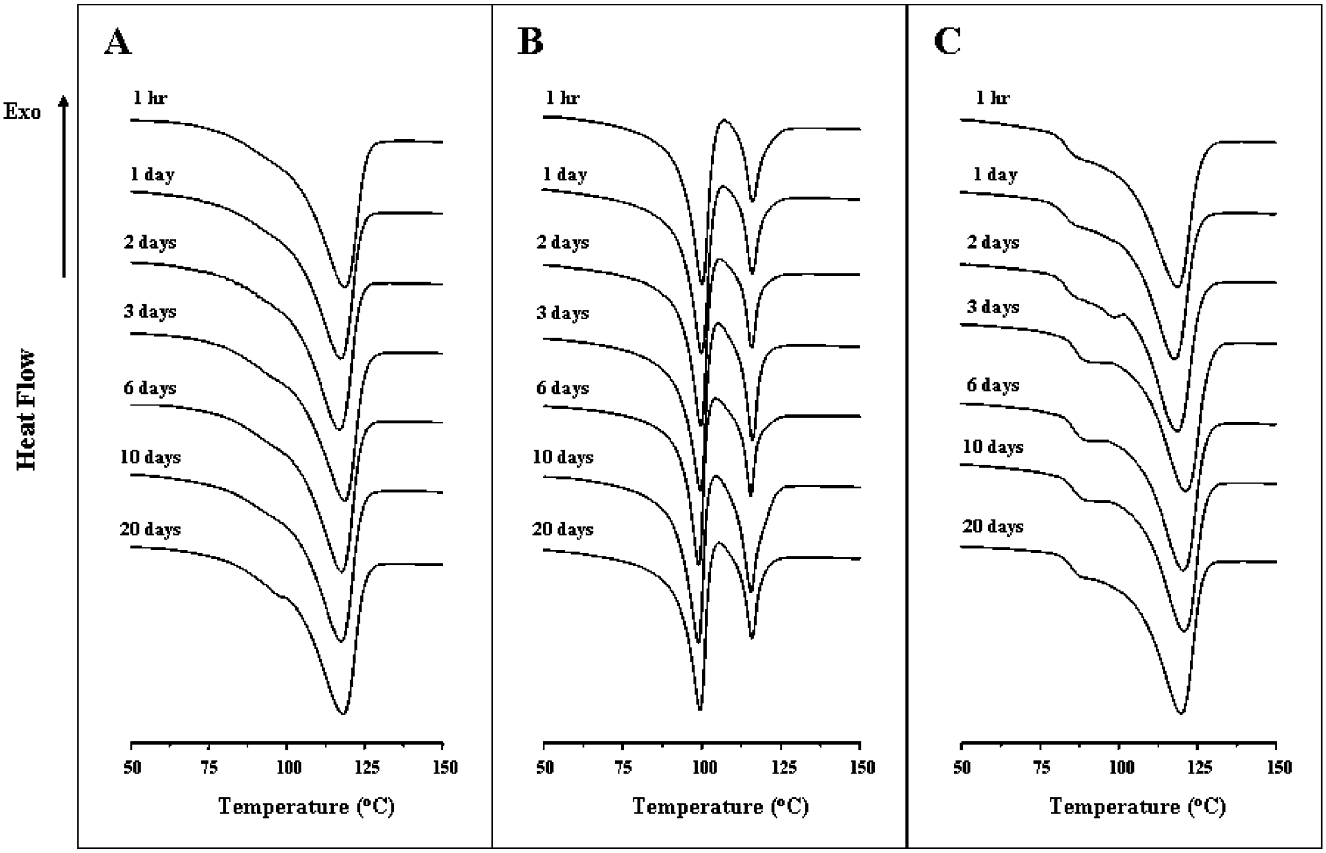
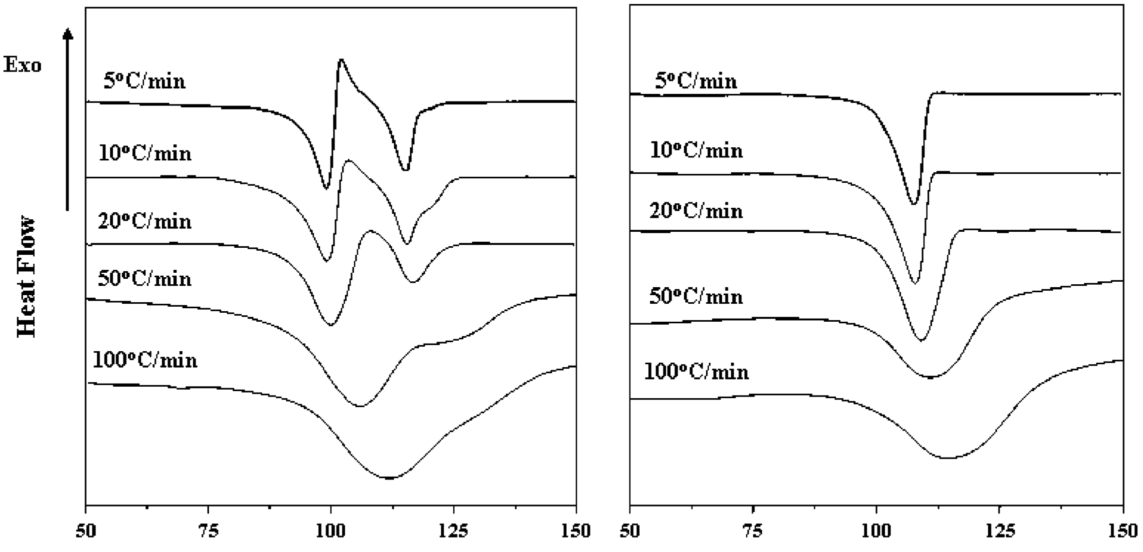


Figure 7. DSC thermograms of (A) the electrospun fibrous membrane, (B) the solvent cast film, and (C) the electrospun heat treated fibrous membrane with aging time.



(A) (B)

Figure 8. DSC thermograms of solvent cast film at various heating rates: (A) first and (B) second heating scans.

different compared to that of the electrospun fibrous membrane due to the presence of a different helical structure. The characteristic bands of form III are present at 296 (CCC bending), 387 (CCC bending), 764 (CH_2 and CH_3 rocking), 778 (CH_2 and CH_3 rocking), 807 (CH_2 rocking and CC symmetric vibration), 818 (CH_2 rocking and CC symmetric vibration), 900 (CH_3 rocking and CH_2 twisting), 1215 (CH_2 twisting and CH wagging), and 1317 cm^{-1} (CH_2 and CH wagging). These Raman results are in good agreement with previous studies.[29]

To further aid in the identification of the crystalline forms present in the samples and to study the crystalline transformation (II → I), WAXD and DSC were employed, and the results are shown in Figures 6 and 7, respectively. As evidenced by WAXD, there exist different crystalline structures for the electrospun fibrous membrane and the solvent cast film (Figure 6).

At an early stage (1 h aging time after electrospinning), the WAXD profiles of the electrospun fibrous membranes clearly show the (100), (300), and (220) crystalline reflections at $2\theta =$

9.9°, 17.2°, and 20.1°, indicative of a hexagonal crystal (form I or I′) and the (200) and (213) crystalline reflections at $2\theta = 11.8^\circ$ and 18.3°, indicative of a tetragonal crystal (form II) (Figure 6A). With increasing aging time, the intensities of the two peaks corresponding to form II decrease but do not completely disappear even after 20 days of aging time, while the intensity of peaks of the hexagonal crystalline form increases.

For the electrospun heat treated fibrous membrane (Figure 6C), a weak peak related to form II at $2\theta = 11.8^\circ$ exists after 20 days of aging time, but the peak at 18.3° is only observed as a shoulder at 1 h aging time. Thus, it is reasonable to assume that this transformation is accelerated by heat treatment. The electrospun fibrous membrane and the electrospun heat treated fibrous membrane both contain hexagonal crystalline structures (form I or I′). Form I and I′ cannot be distinguished by WAXD since they exhibit the same unit cell. However, these forms exhibit different melting temperatures (see Table 1).[9] The melting temperature of the electrospun fibrous membrane and the electrospun heat treated fibrous membrane was found to be 119 °C (Figure 7A). Although the melting point for form I is generally found in the temperature range 120−135 °C, these results indicate that the crystalline structure of the electrospun fibrous membrane is clearly form I. For the electrospun heat treated fibrous membrane, a small shoulder on the endothermic peak was observed at about 85 °C, which seems to be formed by heat treatment.

However, on the contrary, the WAXD profiles of the solvent cast films (Figure 6B) show strong reflections at $2\theta = 12.2^\circ$, 17.1°, and 18.6° and weak reflections at 14.2°, 21.0°, 23.2°, 24.5°, and 27.0° indicative of form III[30] and did not exhibit time dependence. Furthermore, a weak reflection at $2\theta = 9.9^\circ$ indicative of a hexagonal crystal structure exists. This is considered as form I′ because it exhibits an endothermic peak at 99 °C (Figure 7B).

The DSC thermogram of the solvent cast film shows two endothermic peaks at 99 and 116 °C in the first heating scan. The former is the melting of a mixture of forms III and I′, and the latter is the melting of form II formed by the recrystallization during heating (see Table 1). Evidence of the recrystallization can be seen from the exothermic peak at 106 °C in Figure 7B. In order to illustrate that recrystallization occurs, high-speed differential scanning calorimetry (Hyper-DSC) was carried out at various heating rates, and significant differences were observed, as shown in Figure 8. As the heating rate increased, the form II peak corresponding to the recrystallization decreased. Also, the exothermic peak disappeared at heating rates above 20 °C/min. Furthermore, the endothermic peak of form II at heating scan of 100 °C/min exists only as a slight shoulder because there is not enough time for recrystallization to occur during heating. As a result, the crystalline structure of the solvent cast film exhibits a mixture of form I′ and III. However, form III is the dominant structure as evidenced by FT-IR, Raman, and WAXD.

In the second heating scans, the electrospun fibrous membrane exhibits an endothermic peak at 107 °C, while the solvent cast film exhibits an endothermic peak at 108−114 °C depending on the heating rate (Figure 8B). These peaks indicate the melting of form II, which is commonly obtained by recrystallization from the melt. Further evidence of this is seen in the crystallization temperature (T_c) of both the electrospun fibrous membrane and the solvent cast film, which is near 67 °C at the cooling rate of 20 °C/min (data not shown).

Conclusions

We have successfully prepared an electrospun i-PB fibrous membrane from a solution using mixed solvents and examined the crystalline transformation of these fibers by FTIR, Raman, WAXD, and DSC. Although the electrospun fibers and the solvent cast film are both crystallized from the same polymer solution, different crystalline modifications are observed. This is thought to result from different solvent evaporation rates and stresses induced on the charged polymer solution during electrospinning. Recently, it was reported that the γ-conformation of nylon-6 is obtained by stresses induced during electrospinning.[31] For the electrospun fibrous membrane of i-PB, mixed crystalline structures of form I and II exist at an early stage, with the metastable form II gradually being transformed into thermodynamically stable form I. The transformation can be accelerated by heat treatment. On the other hand, a solvent cast film exhibits a mixture of forms I′ and III, with form III being the dominant crystalline structure, as evidenced by FTIR, Raman spectroscopy, DSC, and WAXD.

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