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Electrospinning of Syndiotactic Polypropylene from a Polymer Solution at Ambient Temperatures

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ABSTRACT: A syndiotactic polypropylene (sPP) fibrous membrane was successfully prepared from a multicomponent solvent system at room temperature. As demonstrated by SEM, the morphology of sPP was strongly dependent upon the environment, especially the ambient temperature during electrospinning. The crystal structure of electrospun sPP fibers exhibits a mixture of forms I and III, as determined by WAXD. It is hypothesized that the less stable form III crystals with trans-planar chains are induced in the electrospun sPP fibers due to rapid, stress-induced crystallization during the electrospinning process. To confirm the existence of a trans-planar conformation, FT-IR and Raman were employed. However, it was found that form I is the dominant crystal structure in electrospun sPP fibers.

Introduction

Since polypropylene (PP) was first synthesized by Natta[1] in 1954, it has been of major interest as a plastic and fiber forming material. Commercially, isotactic polypropylene (iPP) having a 3/1 helical conformation in the crystalline phase has been extensively used, owing to a relatively high melting temperature (about 170 °C), compared to syndiotactic polypropylene (sPP).[2] New metallocene catalysts discovered in the 1980s have successfully produced sPP with high crystallinity, high stereoregularity, and melting temperature, and interest in sPP has risen due to its special physical properties, quite distinguishable from those of iPP.[3] sPP is a semicrystalline polymer that presents a very complex polymorphic behavior.[3−5] Four different crystalline forms (I, II, III, and IV) of sPP have been demonstrated and are summarized in Table 1.[3−9]

A number of polymers, both synthetic and natural, as well as biopolymers have been successfully spun into fibers with diameters ranging from tens of nanometers to a few micrometers via electrostatic polymer processing,[10,11] known as “electrospinning”. However, successful spinning of polyolefins, including polyethylene and polypropylene, has been limited due to their high solvent resistance and very high electrical resistivity. Recently, we reported electrospinning studies of polyolefin fibrous membranes prepared from solution at room or slightly elevated temperatures.[12,13] In addition, some researchers have been trying to electrospin fibers with nanoscale diameters from the melt.[14−16]

In this study, we focus on the preparation of sPP fibrous membranes from solution at slightly elevated temperature and a determination of their crystal structure using WAXD, FTIR, and Raman spectroscopy.

Experimental Section

Materials. Syndiotactic polypropylene (sPP, melt index: 4.5 g/10 min at 230 °C with a load 2.16 kg, ASTM D1238) used in this study was purchased from Aldrich. The weight-average (M_w) and number-average molecular weight (M_n) are 127 000 and 54 000 g/mol, respectively ($M_w/M_n = 2.35$). sPP was dissolved in a mixture of cyclohexane, acetone, and dimethylformamide (DMF) (80/10/10 by weight ratio) at 60 °C at a weight concentration ranging from 4% to 5.5% and then cooled down to room temperature for electrospinning. All chemicals were used without further purification. Films were prepared 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 5 mL glass syringe equipped with a 21 gauge needle. A high-voltage power supply (Har-100*12,Matsusada, Co., Japan) was used to generate a potential difference of 10 kV between the needle and an aluminum foil-covered grounded metallic rotating drum placed 15 cm from the tip of the needle.

Characterization. The morphology of the electrospun sPP fibrous membranes was examined with scanning electron microscopy (SEM, VE-8800, Keyence Co., Japan). Wide-angle 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°. To monitor the conformation of the polymer chains via infrared spectroscopy, a Nexus 670 spectrometer (Thermo Nicolet) was used. 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., NJ) using a 785 nm diode laser for excitation.

Results and Discussion

It is possible that sPP may not be appropriate for electrospinning from solution due to the high[1] solvent resistance and resultant high electrical resistivity.[2] Perhaps this explains why polyolefins such as PE and PP have had limited success electrospinning from solution at room temperature.

It is well-known that the morphology of electrospun fibers and spinnability is strongly affected by the electrospinning parameters,

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including solution properties and the surrounding environment.[17] Solution properties can be changed by adding small amounts of nonsolvents. In this study, two types of nonsolvents, acetone and DMF, are used to introduce polarity and volatility to aid in the electrospinning.

SEM images and the frequency distribution of sPP fiber diameters of electrospun fibers prepared under the conditions described previously (5 wt % in 80/10/10, cyclohexane/acetone/DMF dissolved at 60 °C, spun at 35 °C) are shown in parts A and B of Figure 2, respectively. As demonstrated by SEM, fibers with roughened surfaces such as the curled shaped fibers are introduced, and the diameter of each single fiber is not uniform. Also, twisted ribbon-shaped fibers were often observed.

As shown in Figure 3, heterogeneous fibrous membranes composed of nano- and microfibers with two different diameters were observed. Interestingly, irregular microholes on the electrospun sPP microfibers were observed when spinning at lower temperature (20−25 °C). Within the microholes, a number of aligned ultrathin sPP fibers exist (Figure 3B). This is not a well-known phenomenon, and the forming mechanism is not yet clear. However, it is possibly the result of rapid gelation in a heterogeneous system with solvent-rich and solvent-poor regions at lower temperature. When these solvent-rich regions form, the extensional flow induced in the whipping region will tend to elongate the voids in the direction of the fiber axis.

Table 1. Crystallographic Data for Syndiotactic Polypropylene

			unit cell dimension (Å)		
form	crystal lattice	conformation	*a*	*b*	*c*
I	orthorhombic	s(2/1)2	14.5	11.2	7.4
II	C-centered orthorhombic	s(2/1)2	14.5	5.60	7.4
III	orthorhombic	trans-planar	5.22	11.17	5.06
IV	triclinic	$(T_6G_2T_2G_2)_n$	5.72	7.64	11.60

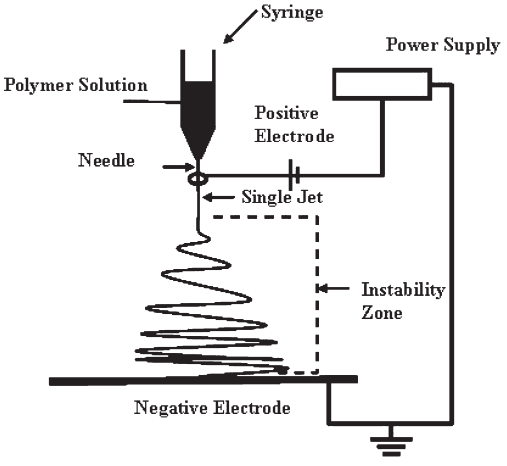


Figure 1. Schematic diagram of the electrospinning setup.

As mentioned in the Introduction, sPP exhibits a complex polymorphic behavior in its crystalline region. De Rosa and Auriemma systemically reported on the structure and physical properties of sPP.[3] Forms I and II are characterized by chains in a helical conformation. Form I is the stable and most common form of sPP obtained by crystallization both from the melt and from solution.[3,18]

Form II, first discovered by Carradini et al. in 1960, is the metastable form and commonly observed in oriented fibers obtained by stretching low stereoregularity sPP.[3] On the other hand, forms III and IV are characterized by chains in the trans-planar and $(T_6G_2T_2G_2)_n$ conformation, respectively. Form III is the less stable form, owing to its higher energy compared to the helical forms I and II.[3] Therefore, form III was observed to transform into form II after removing the stress. Form IV was observed after exposing the stretched fibers of form III to organic solvents such as benzene and toluene.[3]

Films were obtained by solvent casting from the same solution used for electrospinning. The WAXD profile of the solvent-cast film is shown in Figure 4A. The solvent cast film clearly shows the (200), (020), and (121) crystal reflections at $2\theta = 12.2°$, 16.0°, and 20.6°, indicative of form I with an antichiral helical conformation.[6] It is considered as the disordered modification of form I because there is no existence of the (211) reflection at $2\theta = 18.9°$ indicative of structural order found in form I.[2] The WAXD profile of the electrospun sPP fibrous membrane is shown in Figure 4B. The relative intensity of the (200) crystal reflections at $2\theta = 12.2°$, corresponding to form I in the electrospun sPP fibrous membrane, is weaker than that observed for the

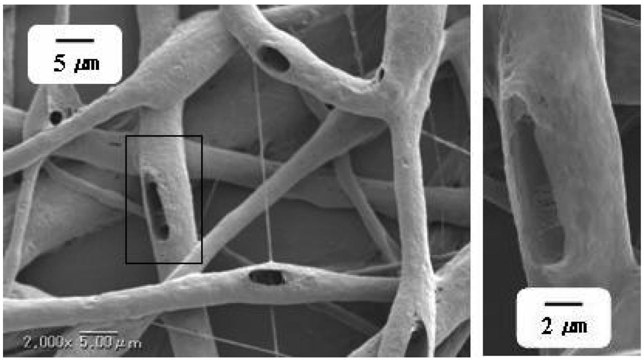
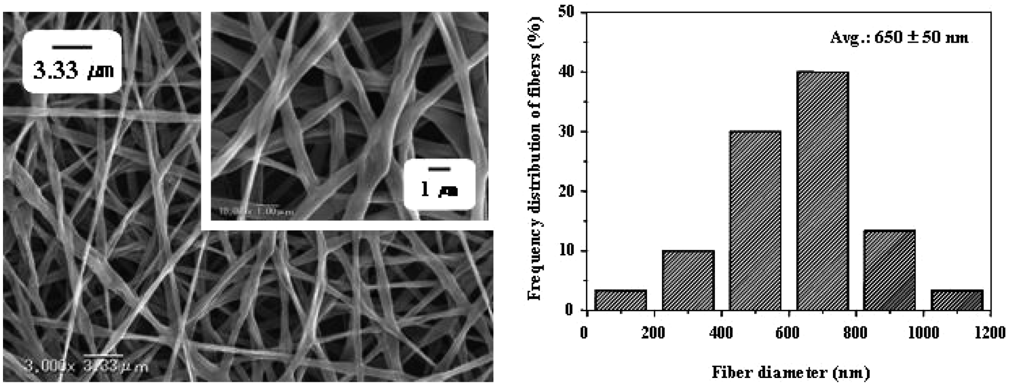


Figure 3. SEM images of electrospun sPP fibrous membrane from solutions at a lower temperature (about 20−25 °C).



(A) (B)

Figure 2. (A) SEM image and (B) frequency distribution of electrospun sPP fibrous membrane from solutions at a slight elevated temperature (35 °C).

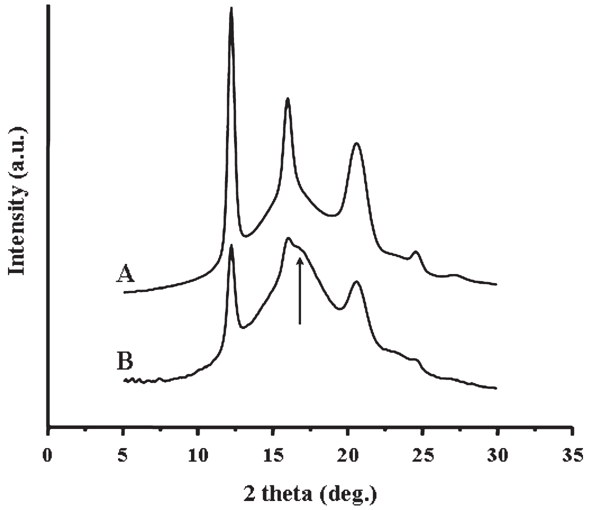


Figure 4. WAXD profiles of (A) the solvent cast film and (B) the electrospun sPP fibrous membrane.

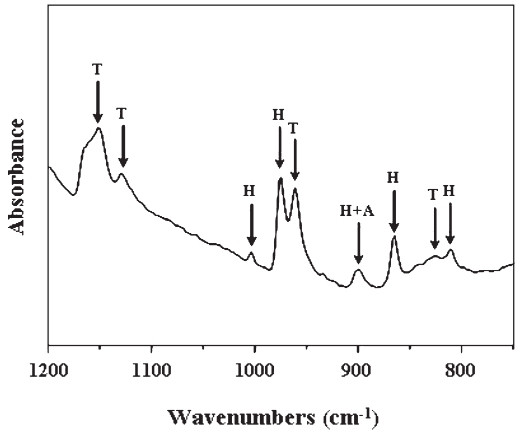


Figure 5. FT-IR spectrum in 750−1200 cm^{-1} region of the electrospun sPP fibrous membrane; H and T indicate helical and trans-planar peaks.

solvent-cast film. It is possible to conclude that there is a slight decrease in the amount of crystalline form I. The disordered modification of form I in the electrospun sPP fibrous membrane is a possibility because of the absence of the (211) reflection at $2\theta = 12.2°$. This may result from rapid crystallization during the electrospining process. Furthermore, a new broad peak centered at $2\theta = 16.9°$ (see the arrow in Figure 4B) appeared. This peak is generally observed in both forms II and III.

To confirm the attribution of this peak, FT-IR and Raman spectroscopy were employed and are shown in Figures 5 and 6, respectively. Both FT-IR and Raman are well-known to be sensitive methods to determine molecular and chain conformation. As mentioned previously, forms I and III have polymer backbones in the helical and the trans-planar conformation, respectively. All bands corresponding to the helical and trans-planar conformation of sPP in the infrared have been assigned previously.[19,21] Recently, Sevegney et al.[21] reported that certain FT-IR bands are sensitive to both the conformation and crystal structure of sPP. In the FT-IR spectrum of the electrospun sPP fibrous membrane, the bands at 811, 866, 976, and 1004 cm^{-1} are indicative of the helical conformation while bands at 827, 962, 1130, and 1151 cm^{-1} are assigned to the trans-planar conformation. According to Sevegney et al.,[21] the band at 902 cm^{-1} is observed in both the amorphous and helical conformation. Furthermore, the intensity of the 962 cm^{-1} is smaller than that of the 976 cm^{-1} band (R962/976 < 1), indicating the existence of a relatively higher content of helical conformation in the electrospun sPP fibers. Also, the existence of the trans-planar conformation in the electrospun sPP fiber is clearly observed in the Raman spectrum (Figure 6). The strong bands at 827, 871, and 963 cm^{-1} and the weak band at 1131 cm^{-1} are representative of the trans-planar conformation.

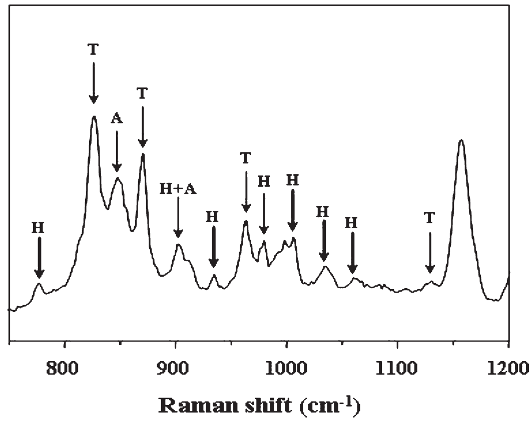


Figure 6. Raman spectrum in 700−1200 cm^{-1} region of the electrospun sPP fibrous membrane; H and T indicate helical and trans-planar peaks.

From these results, we conclude that the crystal structure of electrospun sPP fiber is a mixture of the forms I and III crystalline modifications due to rapid strain-induced crystallization during the electrospinning process. However, form I is the dominant crystal structure of the electrospun sPP fibrous membrane as demonstrated by WAXD.

Conclusions

We have successfully prepared an electrospun sPP fibrous membrane from solution at slightly elevated temperature and examined the crystal structures present in these fibers by WAXD, FTIR, and Raman. Although the electrospun fibers and the solvent cast film are both crystallized from the same solution, different crystal structures are observed. This is thought to result from rapid, strain-induced crystallization during electrospinning. As demonstrated by WAXD, FTIR, and Raman, the electrospun sPP fibrous membrane exhibits a mixture of form I and III crystals, with form I being the dominant crystal structure, whereas a solvent cast film exhibits only the form I crystalline modification.

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