

Effects of the Tacticities of Poly(vinyl alcohol) on the Structure and Morphology of Poly(vinyl alcohol) Nanowebs Prepared by Electrospinning

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ABSTRACT: The effects of tacticities on the characteristics of poly(vinyl alcohol) (PVA) nanowebs prepared by an electrospinning technique were investigated. PVA webs composed of uniform nanofibers with syndiotactic dyad (s-dyad) contents of 53.5 and 57.3% were successfully obtained with electrospinning. By changing processing parameters such as the initial polymer concentration, applied voltage, and tip-to-collector distance, we found suitable conditions for forming PVA webs with uniform nanofibers. PVAs of higher s-dyad contents were prepared at a lower solution concentration and at a higher applied voltage

because of the easy formation of syndiotactic PVA chain entanglements at a very low polymer concentration. The average diameter of the nanofibers in a PVA web with the higher s-dyad content of 57.3% (ca. 240 nm) was thinner than that of the nanofibers in a PVA web with the lower s-dyad content of 53.5% (ca. 270 nm). In addition, the crystallinity and thermal stability were greatly increased with an increase in the s-dyad content. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3282–3289, 2007

Key words: poly(vinyl alcohol); morphology; electrospinning

INTRODUCTION

Electrospinning is a process that produces continuous polymer fibers with nanoscale diameters through the action of an external electric field imposed on a polymer solution or melt.^{1,2} At a voltage sufficient to overcome surface tension forces, fine jets of liquid shoot out toward a grounded target. The jet is stretched and elongated before it reaches the target, is dried, and is collected as an interconnected web of small fibers.³ This process was first studied by Zeleny⁴ in 1914 and patented by Formhals⁵ in 1934. In 1964, Taylor⁶ showed that at a critical voltage, the equilibrium shape of the suspended meniscus is a cone with a semivertical angle of 49.3°. When the applied voltage exceeds this critical voltage, a stable jet of liquid can be ejected. The work of Taylor and others on electrically driven jets of liquid inspired scientists to apply the same principle to various polymeric systems.^{7–11}

Among them, poly(vinyl alcohol) (PVA) has attracted much attention because of its various applications. PVA, obtained by the saponification of poly(vinyl ester)s such as poly(vinyl acetate) (PVAc) and poly(vinyl pivalate) (PVPi), is a linear semicrystalline polymer that is widely used as fibers for cloth and industry, as films, as membranes, and as supporters for medicines. PVA fibers and films are potentially high-performance materials because they have high tensile and impact strengths, high tensile moduli, high abrasion resistance, excellent alkali resistance, and oxygen barrier properties that are superior to those of any known polymer.^{12–14} To maximize these physical properties, the molecular weight, degree of saponification, and syndiotacticity should be increased.^{15–19} In particular, to increase the molecular weight, which is a fundamental factor affecting the physical properties, the improvement of the polymerization method of vinyl acetate (VAc)^{20–22} is necessary.

Generally, PVAc has been used as the precursor of PVA, and atactic poly(vinyl alcohol) (a-PVA) made from PVAc has a poor stereosequences and dissolves in water. Syndiotactic poly(vinyl alcohol) (s-PVA) with high stereoregularity has been made from PVPi with bulky side groups.^{23–26} Because s-PVA has a regular structure and the hydroxyl groups in the main

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chains are alternately arranged, it can easily form strong intermolecular hydrogen bonds.^{27,28} When only PVPi is used as a precursor of PVA, s-PVA does not dissolve in water above 100°C because of the high syndiotacticity.¹⁹ Thus, to prepare water-soluble s-PVA, the molecular weight and syndiotacticity need to be controlled through the copolymerization of vinyl pivalate (VPi) and VAc with various monomer feed ratios and resultant saponification. Because water-insoluble s-PVA is dissolved only in organic solvents, it may cause toxicity in *in vivo* biomaterial uses. However, water-soluble s-PVA can be used for biomaterials with no toxicity. In addition, because water-soluble s-PVA is superior to a-PVA in many physical properties, water-soluble s-PVA can be used to prepare biomaterials with better physical and chemical properties.²⁹

In this study, to consider the effect of the content of the syndiotactic dyads (s-dyads) of PVA on the characteristics of PVA webs obtained by electrospinning, we prepared PVA nanoweb with the same number-average degree of polymerization of 4000 and different s-dyad contents of 53.5 and 57.3% through a series of electrospinning experiments with various process parameters, such as the electrical field, tip-to-collector distance (TCD), and solution concentration. The electrospinning conditions suitable for forming fibrous materials for each were deduced with characterization methods including scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD).

EXPERIMENTAL

Materials

VPi and VAc, purchased from Shin-Etsu (Tokyo, Japan), were washed with an aqueous solution of NaHSO₃ and water and dried with anhydrous CaCl₂; this was followed by distillation in a nitrogen atmosphere under reduced pressure. The initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN; Wako Co., Osaka, Japan), was recrystallized twice in methanol (MeOH) before use. PVA with a number-average molecular weight of 127,000 and a degree of saponification of 88% (Aldrich Co., St. Louis, MO) was used as a suspending agent. Other extrapure-grade reagents were used without further purification. Deionized water was used for all the procedures.

Preparation of PVA

VPi and VAc in definite molar ratios were copolymerized in bulk at 40°C with ADMVN to produce poly(vinyl pivalate/vinyl acetate) copolymers having adequate s-dyad contents for this study. PVA with an s-dyad content of 57.3% was prepared through the

TABLE I
Polymerization Conditions of a-PVA and s-PVA

	a-PVA	s-PVA
Polymerization	VAc bulk polymerization	VPi/VAc bulk copolymerization (2/8 mol/mol feed ratio)
Initiator	ADMVN	ADMVN
Polymerization temperature	40°C	40°C
Saponification solvent	MeOH	MeOH
Alkali solution	NaOH	NaOH

saponification of copoly(vinyl pivalate/vinyl acetate)s. VAc was polymerized in bulk at 40°C with ADMVN to produce PVAc. PVA with an s-dyad content of 53.5% was prepared through the saponification of PVAc. The polymerization conditions are listed in detail in Table I.

Characterization of PVA

The number-average degree of polymerization of PVA was determined by the measurement of the viscosity of a fully acetylated specimen in a benzene solution with an Ubbelohde viscometer (Daihan Scientific, Seoul, Korea).³⁰ The s-dyad content of PVA was determined with a Varian Sun Unity 300-MHz ¹H-NMR spectrometer (Palo Alto, CA), with dimethyl sulfoxide-*d*₆ as the solvent, on the basis of the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm. The degree of saponification was determined by the ratio of *tert*-butyl and acetyl and methylene proton peaks in the ¹H-NMR spectrum. The characteristics of the PVAs are shown in Table II.

Electrospinning of PVA

PVA was dissolved in water at 90°C for 2 h and maintained there for 30 min to ensure homogenization. The concentration of PVA aqueous solutions with an s-dyad content of 57.3% was varied from 0.1 to 1.0 wt %. A PVA solution in a capillary tube, which was fixed above a grounded tubular layer, formed a droplet because of the external nitrogen pressure. With an applied voltage, the droplet was instantly disintegrated into fibers, which were drawn to the tubular layer. The applied voltages ranged from 25 to 40 kV.

TABLE II
Molecular Characteristics of a-PVA and s-PVA

	Concentration of s-dyads (%)	Number-average degree of polymerization	Degree of saponification (%)
a-PVA	53.5	4000	99.9
s-PVA	57.3	4000	99.9

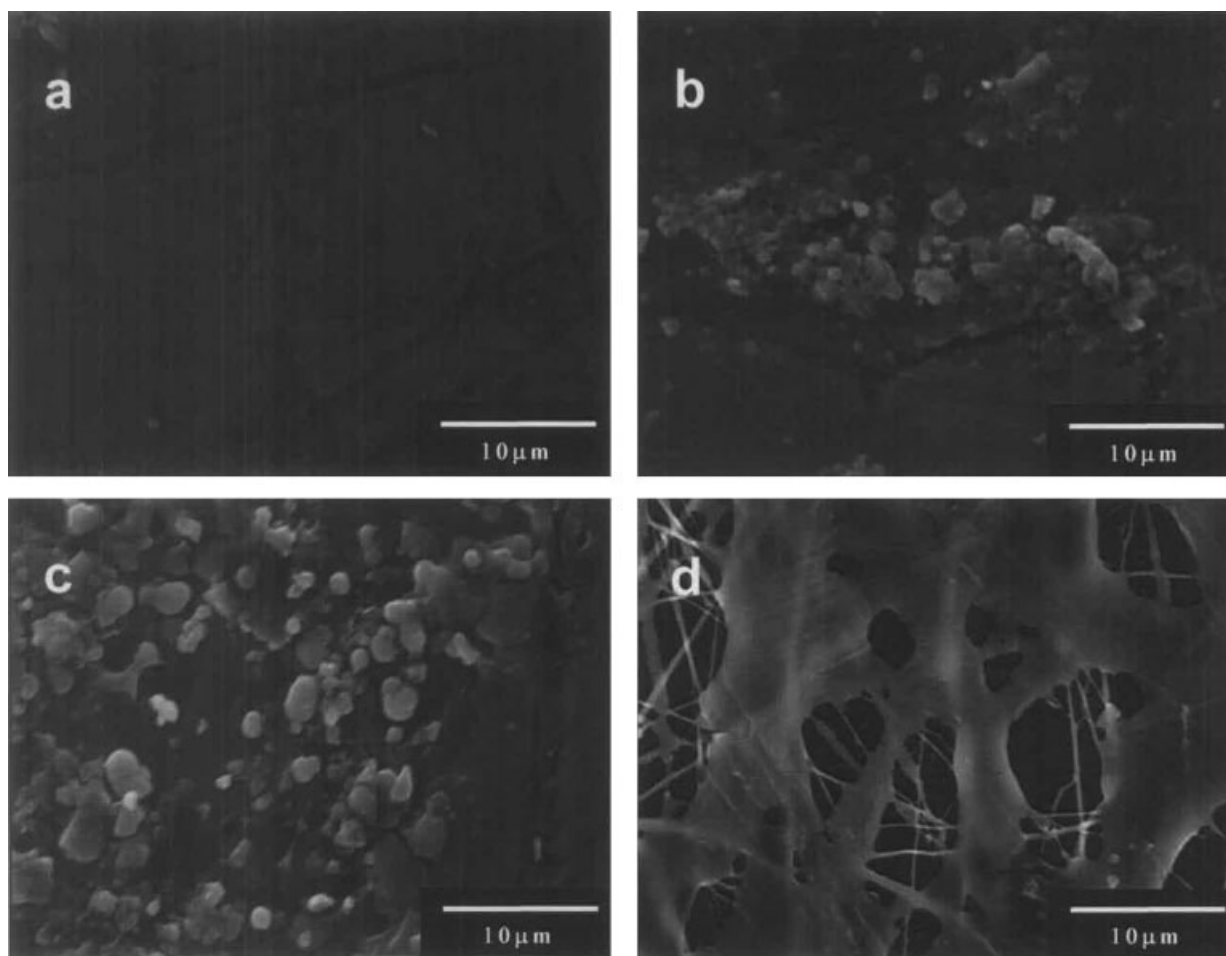


Figure 1 SEM photographs of PVA nanoweb with an s-dyad content of 57.3% electrospun at an applied voltage of 25 kV and a TCD of 15 cm. The polymer concentrations were (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.5 wt %.

TCD was varied from 10 to 20 cm. On the other hand, a PVA aqueous solution with an s-dyad content of 53.5% was electrospun at a polymer concentration of 7 wt %, an applied voltage of 20 kV, and a TCD of 10 cm, which were the electrospinning conditions used to form a fibrous material obtained in a previous study.

Characterization of PVA webs

The fiber morphology and fiber diameter of the PVA nanoweb were determined with SEM. A small section of the fiber mat was placed on an SEM sample holder and sputter-coated with a coating material (platinum) under an argon atmosphere (E-1030, Hitachi, Tokyo, Japan). An accelerating voltage of 15 kV was employed to take the photographs. The crystal melting temperature of the PVA nanoweb was measured with DSC (DSC 7, PerkinElmer, Norwalk, CT) with a sample weight of 10 mg and at a heating rate 10°C/min from 20 to 300°C in a nitrogen atmosphere. WAXD diffractograms were obtained with nickel-filtered Cu K α radiation (26 kV, 6 mA). The measure-

ment of the crystallinity was carried out at room temperature with a Philips X'Pert diffractometer (with a Geiger counter) (Eindhoven, The Netherlands) connected to a computer. The diffraction scans were collected at $2\theta = 3\text{--}40^\circ$.

RESULTS AND DISCUSSION

To choose suitable electrospinning conditions guaranteeing thinner and more uniform PVA nanofibers, we performed a series of experiments in which the electrospinning parameters, including the polymer concentration, applied voltage, TCD, and stereosequence of PVA, were varied.

Figure 1 presents a series of SEM photographs showing changes in the morphology from a bead form to a fiber form, with fiber/bead intermediate stages, during electrospinning at various concentrations. All other parameters were kept constant at an applied voltage of 25 kV and a TCD of 15 cm. The change in the morphology from beads to fibers resulted from a combination of phenomena related to the increase in the polymer concentration. Taylor⁷

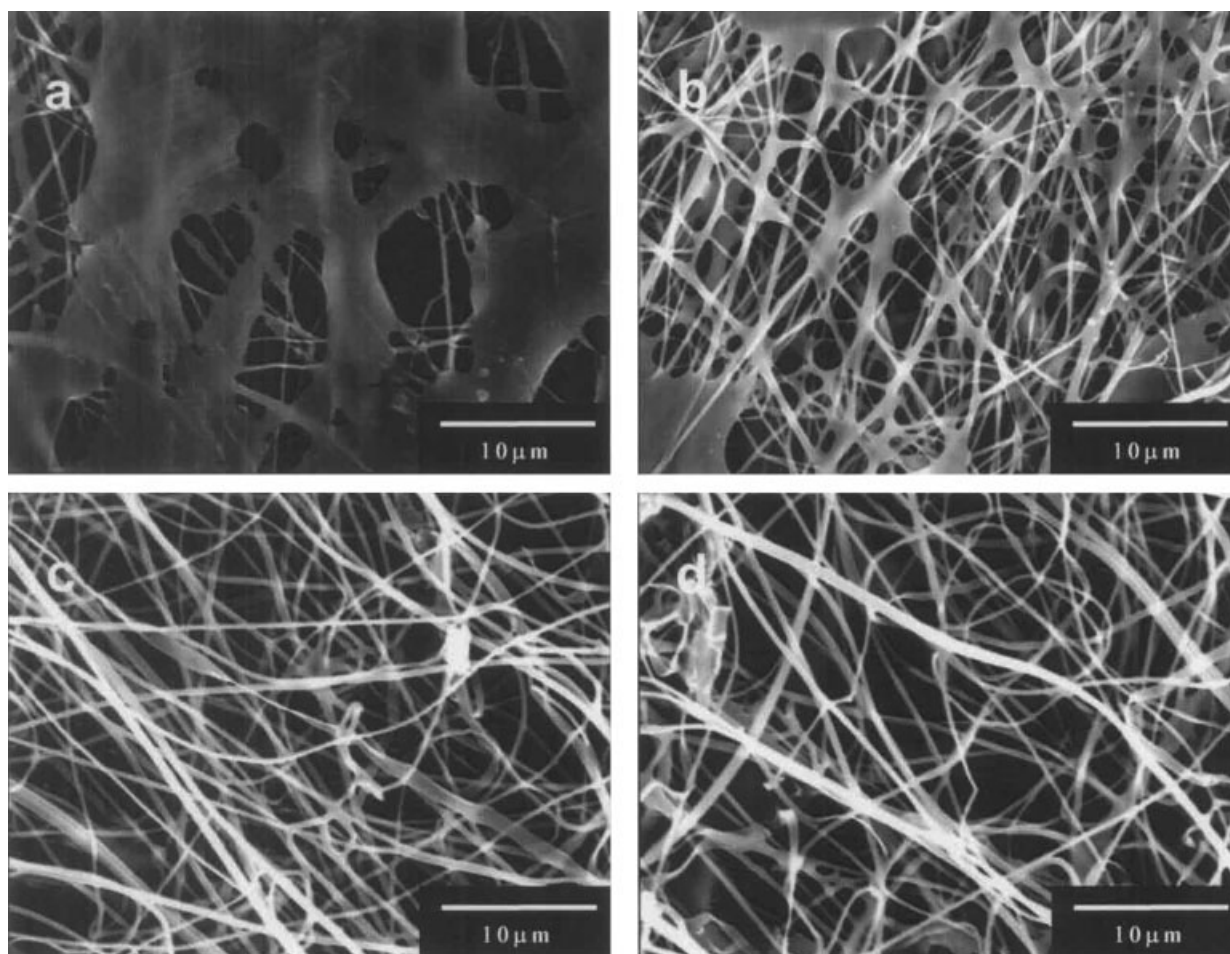


Figure 2 SEM photographs of PVA nanowebs with an s-dyad content of 57.3% electrospun at a TCD of 15 cm and a polymer concentration of 0.5 wt %. The applied voltages were (a) 25, (b) 30, (c) 35, and (d) 40 kV.

observed that in a monomeric fluid, a lower viscosity resulted in the breakup of the electrically driven jet into individual droplets. Consequently, the lowest concentration of the polymer solution was deposited as individual droplets. Similarly, in our study, at polymer concentrations of 0.2 and 0.3 wt %, droplets were formed. At these concentrations, the polymer solution evidently responded to the local changes in electrostatic stresses on the surface of each droplet. These stresses deformed the individual droplets in the same way in which the pendant droplet was deformed by the applied field. However, at 0.5 wt %, there were evidently sufficient molecular chain entanglements in the polymer solution to prevent the breakup of the electrically driven jet and to allow the electrostatic stresses to further elongate the jet. Above a concentration of 0.5 wt %, the solution in the capillary tube did not form a droplet because of sufficient chain entanglements and very high viscosity due to the strong interaction between s-PVA chains by intermolecular hydrogen bonding.

SEM photographs and diameters of PVA fibers prepared when the applied voltage was varied from

25 to 40 kV and TCD was held at 15 cm are shown in Figures 2 and 3, respectively. The fiber morphology is controlled by experimental parameters and is dependent on the solution conductivity, concentration, viscosity, polymer molecular weight, applied voltage, and so forth.^{31,32} Much work has been done on the effects of parameters on the electrospinning process and morphology of fibers. For the effect of the applied voltage, Reneker and Chun³³ found that the fiber diameter did not change much with the electric field when they studied the electrospinning behavior of poly(ethylene oxide). Mo et al.³⁴ and Katti et al.³⁵ reported that the fiber diameter decreased with increasing electrospinning voltage, although the influence was not as great as that of the polymer concentration. However, Demir et al.³⁶ reported that the fiber diameter increased with increasing electrospinning voltage when they prepared polyurethane fibers by electrospinning. In these experiments, the diameter of the fibers collected on the target decreased as the applied voltage was increased because of the increases in the pulling and stretching forces. However, at a higher applied voltage, the diameter of the

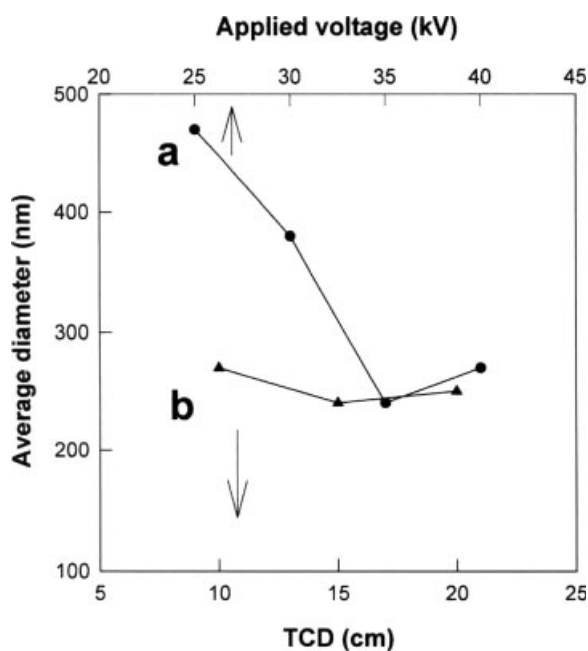


Figure 3 Average diameter of PVA nanofibers in webs with an s-dyad content of 57.3% electrospun at a polymer concentration of 0.5 wt % with various applied voltages and TCDs.

fibers slightly increased. The diameter of fibers is a combined result of both the feed rate and electrostatic force. Increasing the applied voltage increases the electrostatic force and creates a smaller-diameter fiber. However, over a critical applied voltage, it also draws more solution out of the capillary. If a higher electrostatic force draws much more solution out of the capillary, the fiber diameter will increase with increasing applied voltage. On the basis of the results, a web composed of uniform PVA nanofibers can be obtained from a solution with a concentration of 0.5 wt % and an applied voltage of 35 kV.

In the case of TCD, there was no significant effect on the PVA nanofiber morphology with an s-dyad content of 57.3%, as shown in Figures 3 and 4. The SEM photographs were indistinguishable for electrospinning at TCDs of 10–20 cm. It was assumed that the solution jets were elongated and solidified quickly after they flowed out of the needle tip because of the high stereoregularity of the PVA used.

Figure 5 shows SEM photographs of PVA nanowebs prepared under electrospinning conditions suitable for preparing webs composed of uniform PVA

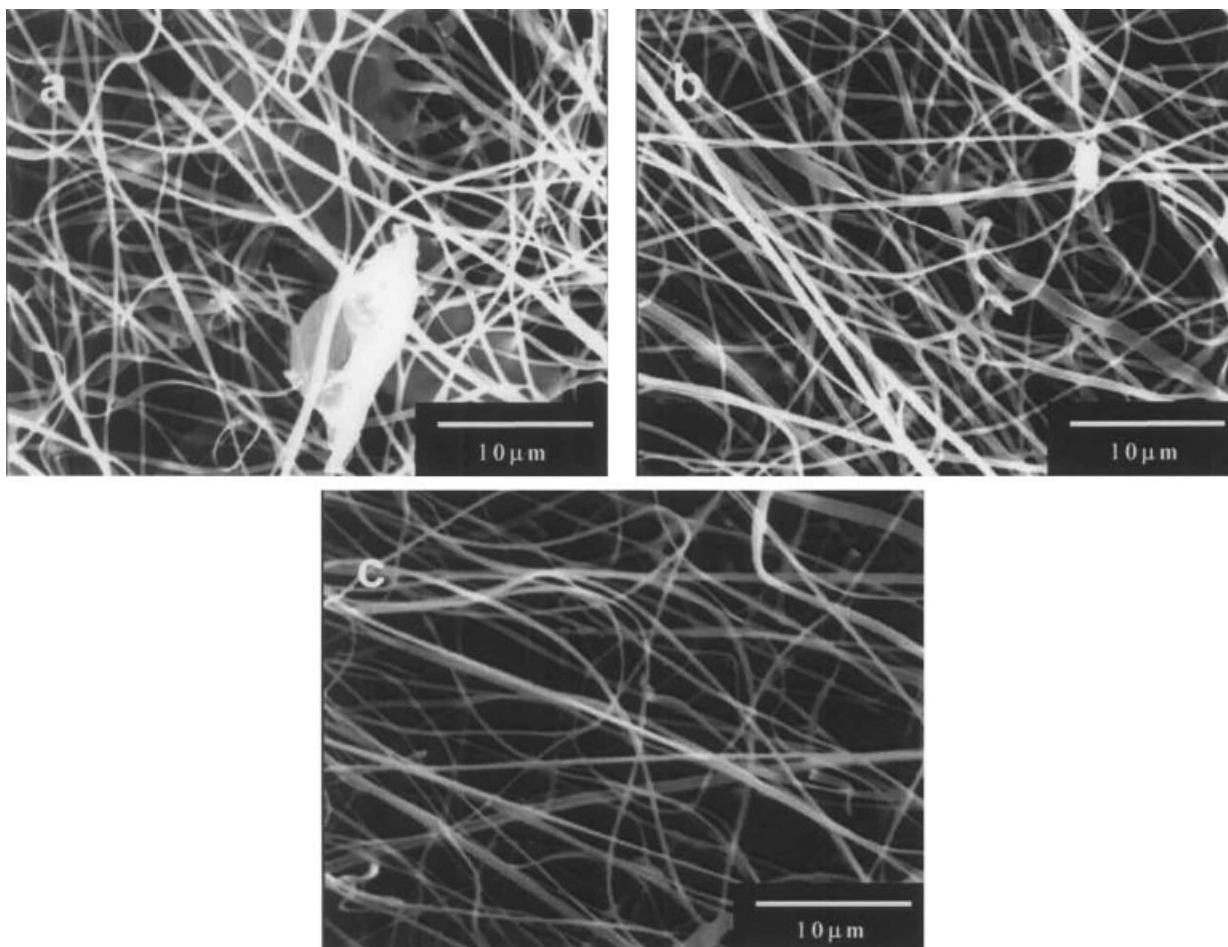


Figure 4 SEM photographs of PVA nanowebs with an s-dyad content of 57.3% electrospun at an applied voltage of 35 kV and a polymer concentration of 0.5 wt %. The TCDs were (a) 10, (b) 15, and (c) 20 cm.

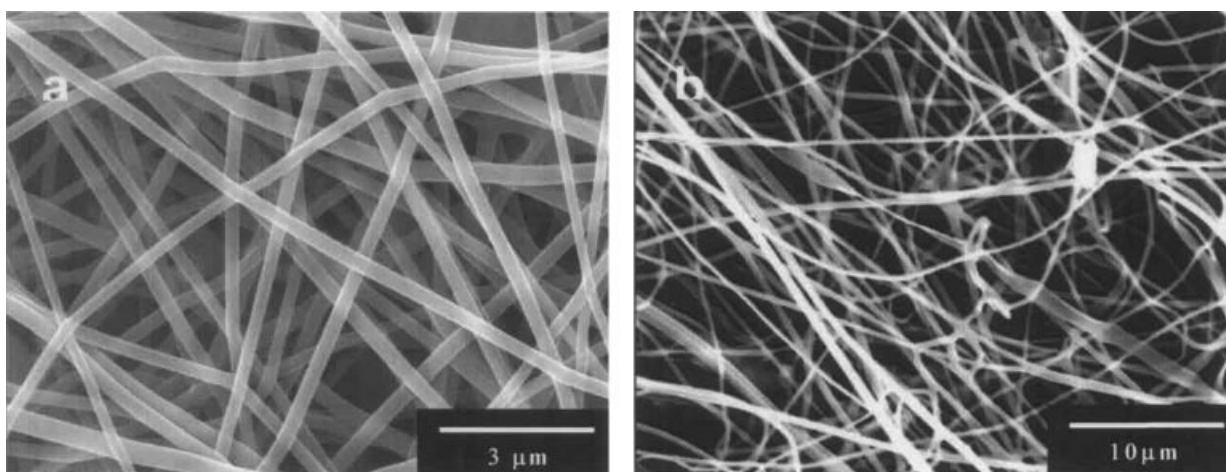


Figure 5 SEM photographs of PVA nanowebs with two different s-dyad contents prepared under suitable electrospinning conditions to form webs composed of uniform nanofibers. The s-dyad contents were (a) 53.5 and (b) 57.3%.

nanofibers. (PVA with an s-dyad content of 53.5% was prepared at a polymer concentration of 7 wt %, an applied voltage of 20 kV, and a TCD of 10 cm. PVA with an s-dyad content of 57.3% was prepared at a polymer concentration of 0.5 wt %, an applied voltage of 35 kV, and a TCD of 15 cm.) The electrospinning conditions used to prepare uniform PVA nanowebs with an s-dyad content of 53.5% were based on previous results.³⁷ Generally, in a polymer solution, both the concentration and molecular weight affect the number of chain entanglements. In addition, in the case of PVA, the stereoregularity significantly affects the number of chain entanglements. Because PVA with an s-dyad content of 57.3% has a more regular structure and the hydroxyl groups in

the main chains are alternately arranged, it is possible to form chain entanglements in a dilute solution. As a result, in a very dilute solution (e.g., 0.5 wt %), a web composed of uniform nanofibers with an s-dyad content of 57.3% is formed.

The individual fiber diameter distributions of PVAs with s-dyad contents of 53.5 and 57.3% are shown in Figure 6(a,b), respectively. There was a decrease in the fiber diameter with increasing s-dyad content. A considerable number of thin fibers with a diameter below 200 nm were found in the PVA with the higher s-dyad content.

Figure 7 shows DSC thermograms of PVA nanowebs prepared under the suitable electrospinning conditions described in Figure 5. In the DSC thermo-

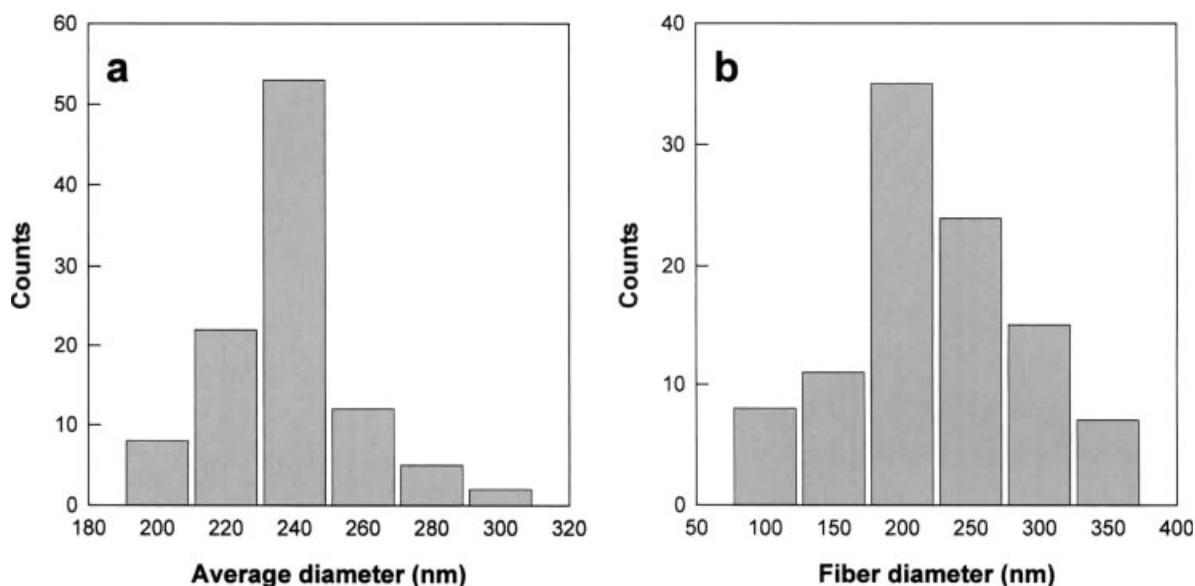


Figure 6 Distributions of diameters of PVA nanofibers in webs with two different s-dyad contents prepared under suitable electrospinning conditions to form webs composed of uniform nanofibers. The s-dyad contents were (a) 53.5 and (b) 57.3%.

gram of PVA with an s-dyad content of 53.5%, two large peaks can be observed at about 100 and 234°C. The endothermic peak at 100°C was assigned to the evaporation point of water during heating, which was also observed for PVA with an s-dyad content of 57.3%. The peak at 234°C was assigned to the melting temperature of PVA with an s-dyad content of 53.5%, which shifted to 251°C for PVA with an s-dyad content of 57.3% because of the higher stereoregularity; this resulted in well-developed crystalline structures and strong intermolecular hydrogen bonding between the adjacent hydroxyl groups.

In investigation of WAXD patterns of PVA fibrils with different stereoregularities, Lyoo et al.³⁸ reported that in the case of PVA fibrils with higher s-dyad contents, the peaks were much narrower and much sharper than those of PVA fibrils with lower s-dyad contents. This explains why larger crystals in the lateral direction can be formed in higher s-PVA. WAXD patterns of the prepared PVA nanowebs are presented in Figure 8. Compared with those of PVA with an s-dyad content of 57.3%, the reflections of the nanoweb pattern of PVA with an s-dyad content of 53.5% were broader. As shown in Figure 8, the crystallinity of the nanoweb with an s-dyad content of 57.3% was much higher than that of the nanoweb with an s-dyad content of 53.5%, notwithstanding the use of the same electrospinning technique and the same drying procedure.

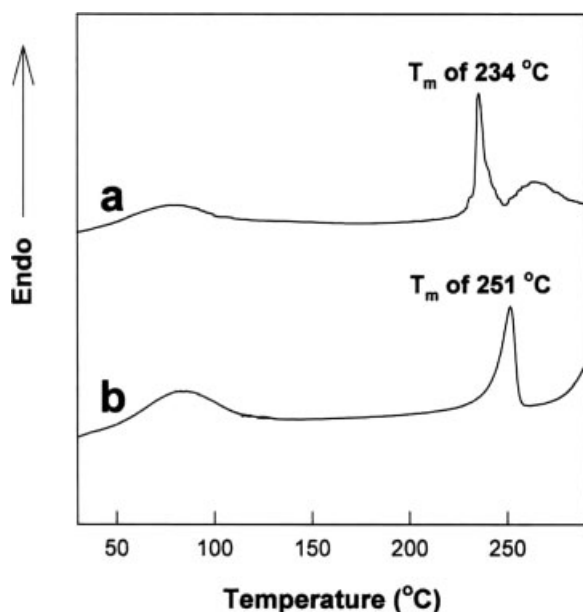


Figure 7 DSC thermograms of PVA nanowebs with two different s-dyad contents prepared under suitable electrospinning conditions. The s-dyad contents were (a) 53.5 and (b) 57.3%. T_m is the melting temperature.

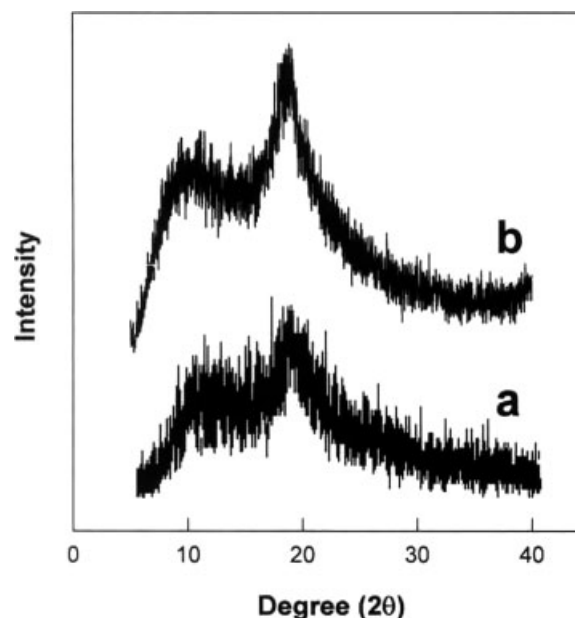


Figure 8 WAXD patterns of PVA nanowebs with two different s-dyad contents prepared under suitable electrospinning conditions. The s-dyad contents were (a) 53.5 and (b) 57.3%.

CONCLUSIONS

The electrospinning conditions used to prepare webs composed of uniform PVA nanofibers were determined through morphological investigations. Under these conditions, PVA nanowebs having average diameters of 270 and 240 nm with s-dyad contents of 53.5 and 57.3%, respectively, were successfully produced. The average diameter of the PVA fibers with an s-dyad content of 57.3% slightly decreased with an increase in the electrical potential and a decrease in the solution concentration. However, above a definite electrical potential, the average diameter of the PVA fibers with an s-dyad content of 57.3% was increased. PVA with the higher s-dyad content could be prepared at a lower solution concentration and at a higher applied voltage because of the formation of chain entanglements at a very low polymer concentration. Also, the PVA nanoweb with the higher s-dyad content showed a crystalline structure and thermal stability superior to those of the PVA nanoweb with the lower content. In the near future, we will report on the preparation of PVA nanowebs with s-PVA/a-PVA blends.

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