Alignment of Electrospun Polystyrene with an Electric Field

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ABSTRACT: Polystyrene (PS) with a concentration of 20% by weight in THF/DMF was electrospun on a flat sheet collector. At a concentration of THF above 75%, blocking at the needle tip caused bead formation. However, a nice fiber mat was obtained with the 75/25 THF/DMF. Moreover, at a traveling distance of 10 and 15 cm and voltages from 10 to 16 kV, the PS fibers exhibited alignment. This alignment was reproducible when voltage stabilizer was connected to the voltage supply. This suggested that the uniformly positive charges arising from external voltage interacted with the aromatic rings on the PS chain, yielding a uniform dipole moment. As a result, during jet traveling, the solvent evaporated and the molecules were oriented and frozen at the ground collector. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3648–3652, 2007

Key words: electrospinning; PS electrospun; aligned electrospun fiber; electric field; induced dipole

INTRODUCTION

Electrospinning is a process to produce fiber in a diameter range of submicrometers to nanometers. The procedure involves applying a high voltage to a capillary and pumping a polymer solution through it. The electric field causes the protruding droplet of polymer solution to deform due to electrostatic forces and causes the hemispherical droplet to become conical in shape, referred to as a Taylor cone. When the critical voltage is reached, the repulsion charge accumulated on the surface of the droplet overcomes the surface tension, and an elongated fiber is forced downward to the grounded target. As the fiber travels toward the target, the solvent evaporates and the fiber is typically dry when arriving at the target. Electrospinning is derived from electrospraying, hence unexpected phenomenon, and experimental results such as the formation of beads, necklaces, etc can be formed.[1] However, with an optimum condition, a nice nonwoven fiber mat is obtained. This electrospun fiber exhibits high surface area and an interconnected fibrous network desirable for a range of applications including textiles, filter systems, chemical/biological resistant protective clothing, tissue engineering, and electronic applications.

Amorphous polystyrene (PS) being a transparent and colorless material is one of the most useful plastics. It has very high electrical resistance and low dielectric loss. Also, it is hard and stiff, but brittle.[2] It is widely used for insulation and packaging materials.[3] PS can be chemically modified[4,5] through aromatic and alkane chemistry for desired applications such as enhanced adhesion,[6] and through copolymerization with polar polymers for the sensing applications.[7,8] Electrospun PS has been reported[1,9,10] in various organic solvents, producing various kinds of morphology.[2,11] Lee et al.[1] reported the formation of beaded fiber in the mix solvent of THF/DMF and revealed that the size of the beads depended on the ratio of the solvents, while Shin et al.[9] reported electrospun recycled PS in DMAc solvent. Although Jarusuwannapoom et al.[10] studied electrospun PS in THF, and the results were quite different from our results.

The interaction between matter and magnetic or electric fields is well known. Melt PS swelled after extrusion in the present of a magnetic field.[12] Recently many researches were carried out to find ''smart materials'' that can respond to electric fields, such as polymer gels used for artificial muscle[13] and amorphous polar polymers used for piezoelectric material.[14] The interaction of matter with an electric field occurs in either of the two ways: as conduction

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or as polarization.[15] Charges which are free to move through the sample show up as a conduction term. If their motion is blocked, the response appears as polarization. With these interaction phenomena, shape or mobility of materials can be observed. For neutral polymers or polymers with low dielectric constant, shape or mobility can be induced by incorporation with polarizable particles[16–19] or dielectric solvents. This effect is called the electrorheological (ER) effect.

Electric fields through external voltage are also involved in the electrospinning process by introducing a positive charge to the polymer solution. Once the repulsion of the charge in the solution overcomes its surface tension, a solution jet is produced. This article discusses the electrospinning of PS in (75/25) THF/DMF and illustrates the interaction of positive charges arising from external voltage with aromatic rings in the PS molecules during electrospinning. As a result, a dipole moment on the PS chains is formed, producing molecular alignment of electrospun fiber on a flat sheet collector.

EXPERIMENTAL

PS with a M_w of 280,000 was purchased from Aldrich. Tetrahydrofuran (THF) and *N*,*N*′-dimethylformamide (DMF) were purchased from Duksan Chemical and Aldrich, respectively. PS was dissolved in THF or in a mixed solvent of THF/DMF with the ratio of 75/25 to obtain a concentration of 20% by weight.

Electrospinning

The electrospinning set-up consisted of a plastic syringe (5 mL) and a needle (0.41-mm i.d.). The needle was connected with a high voltage power supply (Chungpa EMT, Korea). The ground electrode was aluminized on a flat sheet. Typically, electrospinning was performed at a voltage of 8–16 kV and the distance between the capillary tip and the ground collector, so-called traveling distance, was 7–20 cm. The flow rate of the solution was controlled by a syringe pump (Kd Scientific series 100, USA) to maintain at 0.5 mL/h from the capillary outlet. All the experiments were carried out at temperature range of 19–24°C and a humidity of 15–25%.

Scanning electron microscope

Electrospun fibers were coated with gold using sputter coating, and their morphology was observed under scanning electron microscope (SEM; model: JSM-5410, JEOL) with an accelerating voltage of 20 kV and a magnification of 1000. An optical microscope was also used for the morphological scan.

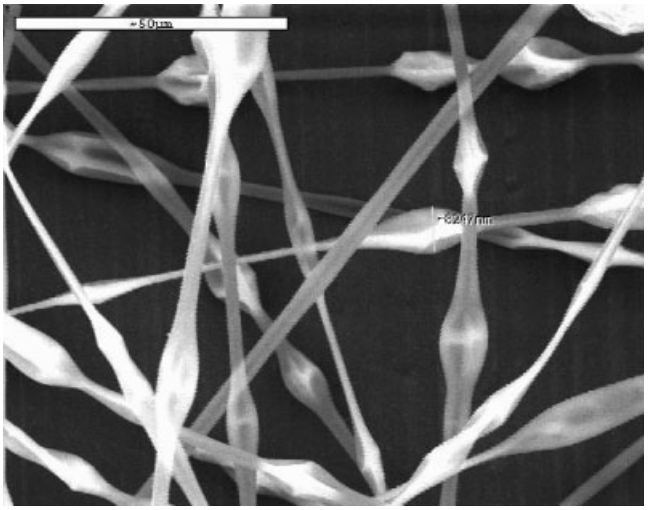

Figure 1 Beads on electrospun PS fiber at 10% by weight in THF.

RESULTS AND DISCUSSION

Electrospun PS in THF has been reported previously. Lee et al.[1] revealed that at a concentration of PS below 15% by weight, beaded fibers were formed, while Jarusuwannapoom et al.[10] reported well-formed fibers with both 10 and 20% concentrations. However, we found a lot of beads on a fiber with the concentration at 10%, shown in Figure 1. The difference of these experimental results might be due to the differences in processing conditions and system conditions, such as molecular weight distribution, temperature, humidity, etc. The temperature and humidity in our experiment were quite low. Moreover, from the optical microscope observations on electrospun PS produced from 20% PS in THF, two areas can be seen, one area having nice fibers and another area having beaded fibers which correspond to those reports.[1,2,10] The beads might come from the block at the capillary tip and web between needle tip and collector, as shown in Figure 2. This is due to the low boiling point of the solvent. To solve this problem, a high boiling point solvent, DMF, was mixed. It was found that at the content of DMF below 25 pph, and the block at the capillary tip maintained. Hence, 20% PS in 75/25 THF/DMF was electrospun with a varying voltage from 8 to 16 kV and a traveling distance from 7 to 20 cm. It was found that at all voltages with a traveling distance of 10 cm, a nice fiber was obtained with a small amount of beaded fiber, as shown in Figure 3. In attempts to increase or decrease traveling distance, more beaded fibers were found. This suggested that, at an excessive traveling distance, static attraction between positive charge jet and ground target was low and the fiber solidified during traveling to the target, On the other hand, with a

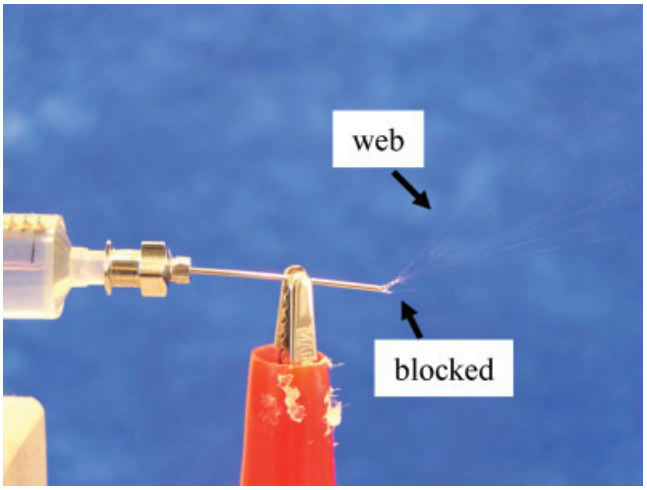

Figure 2 A block at the needle tip and web from needle tip to collector during electrospinning of 20% PS in THF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

very close traveling distance, the jet had no time to elongate, and then a beaded fiber was formed.

Aligned electrospun nanofiber is a way to prepare new anisotropic materials. It can be applied as nanoyarn, reinforced materials and composite materials. This alignment fiber can be produced using ground collector as a high rotating speed drum,[20–22] a disk,[23] or a dual collector.[24] There are no reports about alignment on a flat sheet collector, only randomly deposited on target. Surprisingly, we first found aligned PS electrospun fiber at a distance of 15 cm and a voltage of 13 kV. Attempts to repeat this phenomenon gave a nonwoven mat. Obviously, when the external voltage was stabilized using voltage stabilizer, we found interesting phenomena.

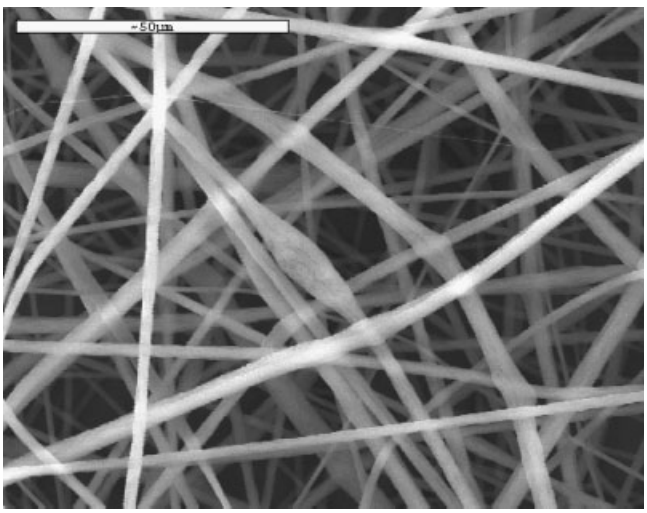

Figure 3 Beaded fiber defect in electrospun PS fiber at 20% by weight in THF/DMF 75/25.

First, perfect fibers were obtained in all experimental parameters, voltages of 10–18 kV, and travel distances of 10–15 cm. Second, aligned PS electrospun fibers were reproducible. Third, the higher the voltage applied, the more aligned fiber area was found, as shown in Figure 4. Figure 4(a) PS was electrospun at 13 kV. The alignment was indicated by the arrows, while other parts were partial aligned or nonaligned. Figure 5 showed the morphology of aligned fibers and randomly or nonaligned fibers. When the voltage was increased to 16 kV [Fig. 4(b)], all fibers were aligned within 20 cm length. We postulated that the alignment might be due to the interaction between aromatic ring on the polymer chain and electric field.

It was reported that the electric field enhanced recrystallization of syndiotactic PS in some typical solvents, such as benzene or toluene.[25] This was due to the electric field caused rearrangement of aromatic ring in PS chain along the benzene ring of the solvent. Chen and Shew[26] reported that PVDF behaved as a polyampholyte, consisting of both negative- and

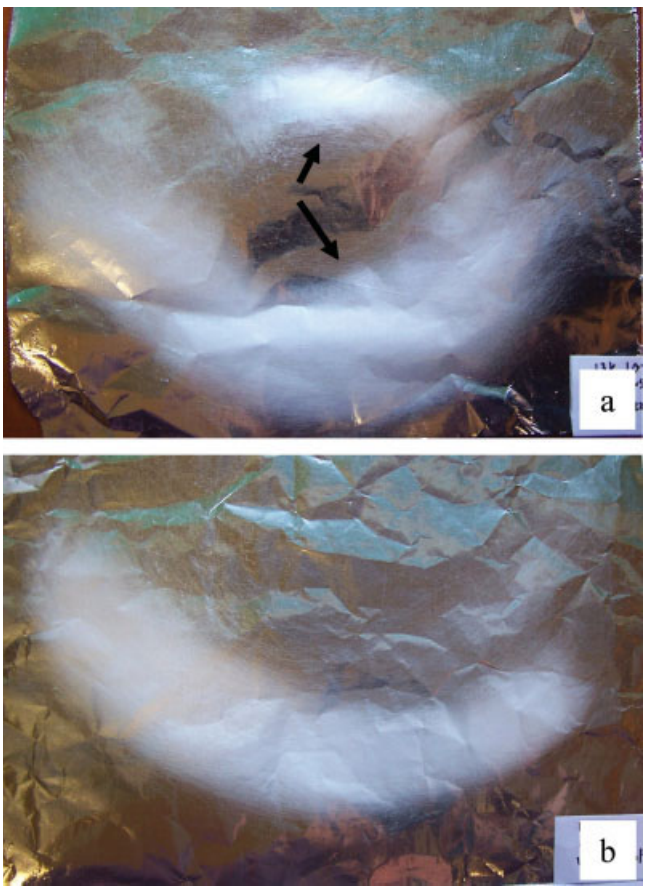

Figure 4 Aligned electrospun PS mat deposited on aluminum foil on a flat sheet collector for 10 min at a condition of (a) 13 kV, 15 cm; (b) 16 kV, 15 cm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

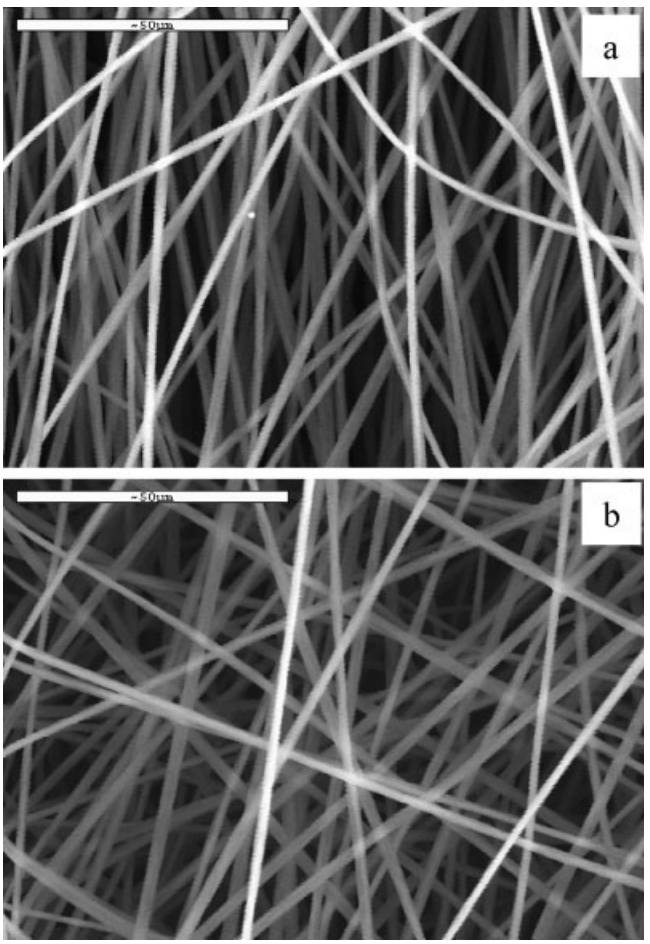

Figure 5 SEM morphology of electrospun PS on a flat sheet collector at a condition of 13 kV and 15 cm: (a) aligned fibers, (b) randomly deposited fiber.

positive-charged monomer in a chain molecule, in dielectric solvents. Hence, in the presence of an external electric field, the solvent-induced molecular conformational deformation in response to the applied field caused the alignment (ER effect) of intrinsic dipoles arising from opposite charges within PVDF molecule. The dipole moment might be along the carbon chain or localized at distortion site.[27] Although the induced dipole of PVDF has been reported,[26] we could not see any alignment of electrospun PVDF on the aluminum flat ground collector. Other materials that could perform ER effect included conjugated polymers[28] and derivatized polymers possessing polar groups such as amino (—NH_2),[29] hydroxy (—OH), and cyanoamino (—NHCN). Carbon nanotubes[30] and carbon nanofibers[31] also demonstrated ER behavior, and hence they can align in epoxy resin during curing under electric field, yielding anisotropic epoxy. Moreover, Park and Robertson[19] found that under an electric field, glass spheres in polymer solutions aligned themselves when the spheres had a narrow size distribution. The longer the electric field was applied, the thicker the alignment of the spheres was. These literatures show that materials can be polarized under electric field, depending on polarity of the materials. Hence, we believed that alignment of electrospun PS on a flat ground collector came from the interaction between the positive charge arising from external electric field and electron in aromatic ring of PS chain, resulting in the chain elongation and alignment. Moreover, the solvent evaporates during the jet travels to the collector. Hence, the alignment of the dipole molecules may be frozen, resulting in the partial orientation,[18] as seen in Figure 4(a). In addition, the higher the external voltage applied, a higher interaction between positive charge and aromatic ring was carried out and a bigger area of alignment of electrospun was formed. That the voltage stabilization gave reproducible results possibly due to the voltage supply exhibited a narrow distribution voltage, thus uniform positive charges reacted with aromatic ring in PS chain, yielding uniform dipole of aromatic rings, which were frozen during the jet traveled to the ground collector.

CONCLUSIONS

Attempts to electrospin on 10 and 20% PS in THF were not successful. Beaded fibers were found along the fibers. Blocking at the needle tip was also a problem. To facilitate electrospinning, a high boiling point solvent, DMF, was added at a level of 25% to the mixed solution. As a result, a well-formed electrospun fiber mat was obtained. Moreover, the fibers were found to be aligned, which was not possible for electrospun on a flat sheet collector. This suggested that the positive charges arising from the external electric field interacted with electrons in the aromatic ring, causing dipoles on the PS chain. While the solution jet traveled to the collector, solvent evaporated. Hence, the alignment of the dipole molecules may be frozen, resulting in the partial orientation. The higher the external voltage was applied, a higher interaction between positive charge and aromatic ring occurred, and a bigger area of alignment of electrospun fiber was obtained.

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