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The change of bead morphology formed on electrospun polystyrene fibers

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Abstract

Polystyrene (PS) dissolved in the mixture of tetrahydrofuran (THF) and *N*,*N*-dimethyl formamide (DMF) was electrospun to prepare fibers of sub-micron in diameters. Electropinning parameters such as polymer concentration, applied voltage and tip-to-collector distance were controlled. From these parameters it was determined that while the surface tension of polymer solution had linear correlation with the critical voltage, throughput was dependent on electric conductivity. The electrospun PS fibers produced contained irregular beads and electrospinning certainly was enhanced with increasing DMF content. The bead concentration was also controlled by DMF content. The aspect ratio of the formed beads and the diameter of fibers were increased with increasing solution concentration. When PS was dissolved in only THF, an unexpected half hollow spheres (HHS) structure appeared. Also, different shape forms of PS non-woven mats have been prepared by controlling electrospinning parameters.

Keywords: Polystyrene (PS); Electrospinning; Morphology

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1. Introduction

Amorphous polystyrene (PS), being transparent, colorless and brilliant material, is one of the most useful plastics. It has very high electrical resistance and low dielectric loss. Also, it is hard, stiff and very brittle. However, variation such as high impact polystryrne (HIPS), which is a copolymer with an elastomeric polymer such as polybutadiene [1,2] are also often used. With regard to this, generally a brittle PS can be made into having certain degree of flexibility by fiberization. Polymer fibers have been produced by electrospinning and traditional methods such as melt, wet and dry spinning. In the past decade, interest in electrospinning process have been arisen, because polymer fibers prepared by this technique were able to achieve fiber diameters in the range of nanometer to a few micrometers [3–10]. An electrostatically driven jet of polymer solution and melt is used in electrospinning. This technique has been introduced by Formhals in 1934 [11]. Despite such advantages can be offered by electrospinning, there is yet no known commercial process available. One reason for this is the inherent low throughput of this process, broad distribution of fiber diameters produced, poor, non-uniform and difficult-to-reproduce mechanical properties as many parameter needs to be controlled during processing.

In electrospinning, unexpected phenomenon and experimental results such as the formation of beads, necklace, ribbon-like and branched jet, etc. [12–15] were reported to occur. The formation of beads within electrospun fibers has been observed often [12,16]. Entov [17] reported that the bead formation occurs as a result of instability of the polymer solution jet. Reneker [12] on the other hand indicated that solution viscosity, surface tension and net charge density induced by the electrospinning are the main factors in the formation of beads during the formation of electrospun fibers. Bead generation is preferred at low concentration polymer solution while higher concentrations lead to the fiber formation.

Mats composed of electrospun nanofibers have a large specific surface area and very small pore size compared to commercial mats. It therefore was used in variety of applications such as filteration [18], protective clothing [19], fiber reinforcement in composite materials [20], and biomaterial field including wound dressings and drug

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delivery systems (DDS) [6] as well as scaffold in tissue engineering [10].

The goal of this study is to prepare electrospun PS fibers having different bead dimensions and shapes, also to characterize such differences in bead formation via controlling various parameters.

2. Experimental

The amorphous PS with number average molecular weight of 140,000 was purchased from Aldrich (Milwaukee, USA). The different concentration polymer solutions for electrospinning were prepared by using mixture of solvents tetrahydrofuran (THF) and *N*,*N*-dimethyl formamide (DMF) in the ratios 100/0, 75/25, 50/50, 25/75 and 0/100 (v/v).

A variable high voltage power supply (CPS-60 k02v1, Chungpa EMT, Co., Korea) was used to produce voltages ranging from 0 to 50 kV. The polymer solution was poured into the 5 ml syringe attached to it a 1 mm diameter capillary tip, and the polymer solutions were delivered to the 5 ml syringe by using a microsyringe pump. The high potential electrode of the power supply was connected to a copper wire inserted into the polymer solution, and the ground electrode to the collector which is a rotating metal drum wrapped with aluminum foil. Device for electrospinning is shown in Fig. 1.

The electrospun samples collected were placed in a vacuum oven for 24 h at room temperature in order to remove the solvent residuals. The applied voltage, tip-to-collector distance (TCD) and polymer concentration were increased in steps of about 3 kV, 3 cm, 3 wt%, respectively.

Surface tension of polymer solution was determined by the Wilhelmy plate method by using Tensiometer (K10ST, Kruss Co., Germany) at 25 °C. The platinum plate of the Tensiometer was cleaned with a butane torch. The viscosity of polymer solution was determined by using Brookfield digital viscometer (Model DV III, USA) at 25 °C. Conductivity of polymer solution was measured by electric conductivity meter (G series, CM-40G, TOA Electronics Ltd., Japan). The morphology of the electrospun fibers was examined with scanning electron microscopy (SEM, GSM-5900, Jeol. Co., Japan). The diameter and distribution of the bead were obtained by using image analyzer (Image-proplus, Media Cybernetics Co., USA).

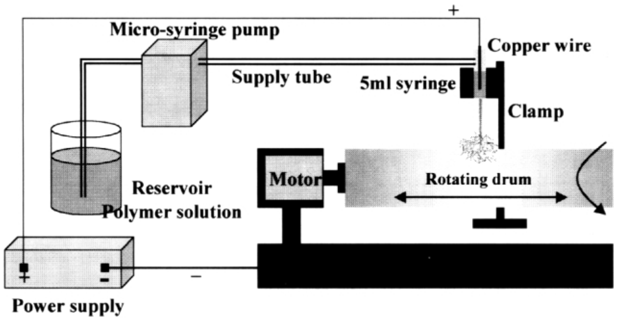


Fig. 1. Device for the electrospinning.

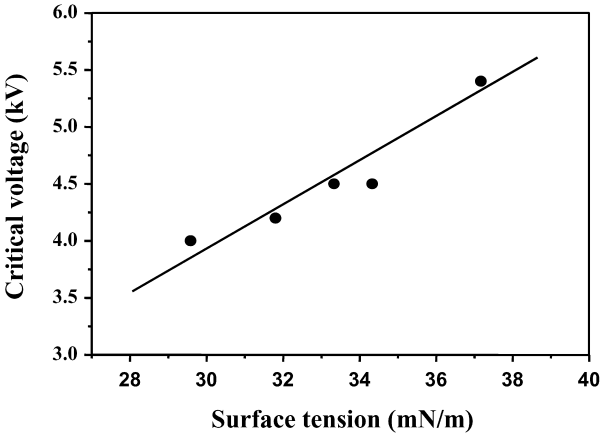


Fig. 2. Plot of the critical voltage versus the surface tension for 13 wt% PS in THF/DMF ratios from 100/0 to 0/100 (v/v).

3. Results and discussion

In the electrospinning, an electrically charged jet of polymer fluids is created by a high voltage power supply. The hemispherical shape of pendant droplet at the end of capillary tip was changed into a conical shape with increasing voltage, which is known as the Tayler cone [21]. If the applied voltage reaches a critical value, a charged jet of polymeric fluids initiates electrospinning toward the collector. This critical voltage is closely related to the surface tension of polymer solutions and for PS dissolved in the mixture of THF and DMF, it tends to increase linearly with surface tension (Fig. 2). In other words, the higher surface tension, the higher applied voltage is required to initiate the jet formation.

Viscosity is the characterization of the intermolecular interactions in polymer solution. The intermolecular

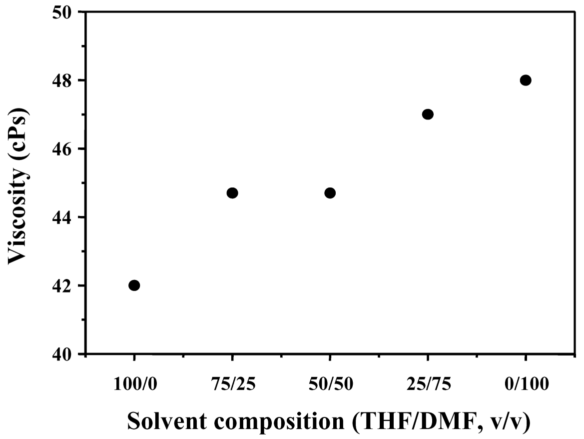
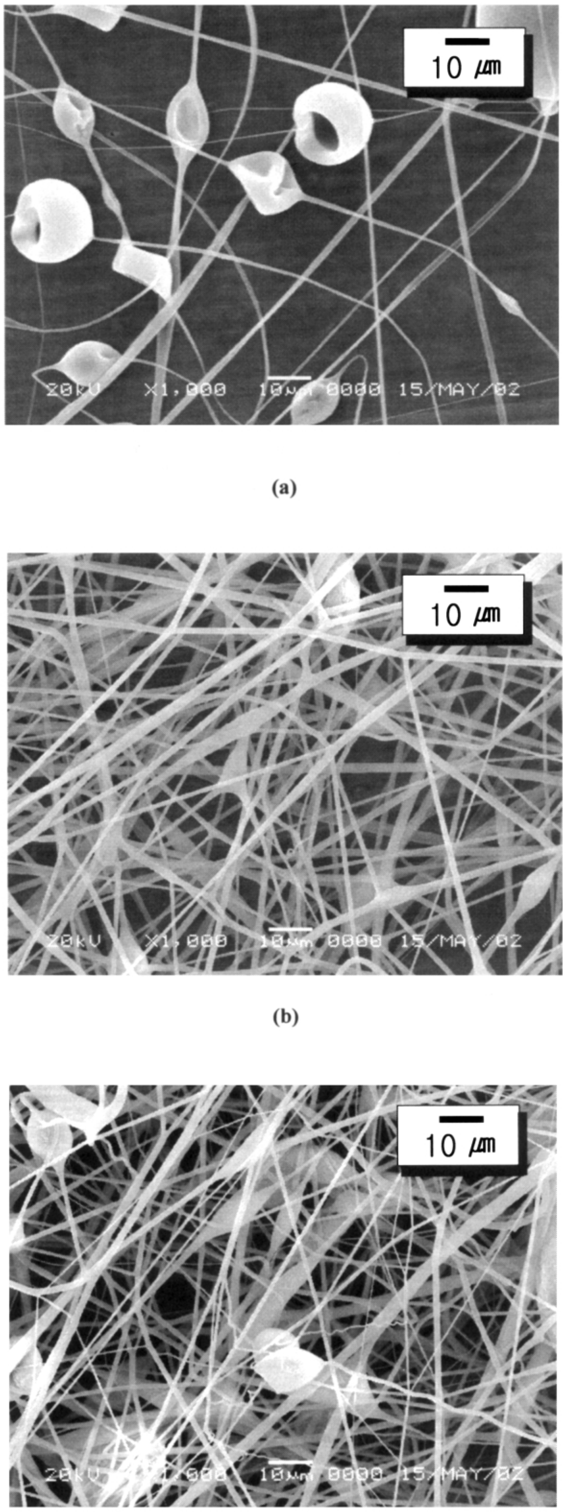


Fig. 3. Solution viscosity as a function of the solvent composition for 13 wt% PS in THF/DMF, (v/v).

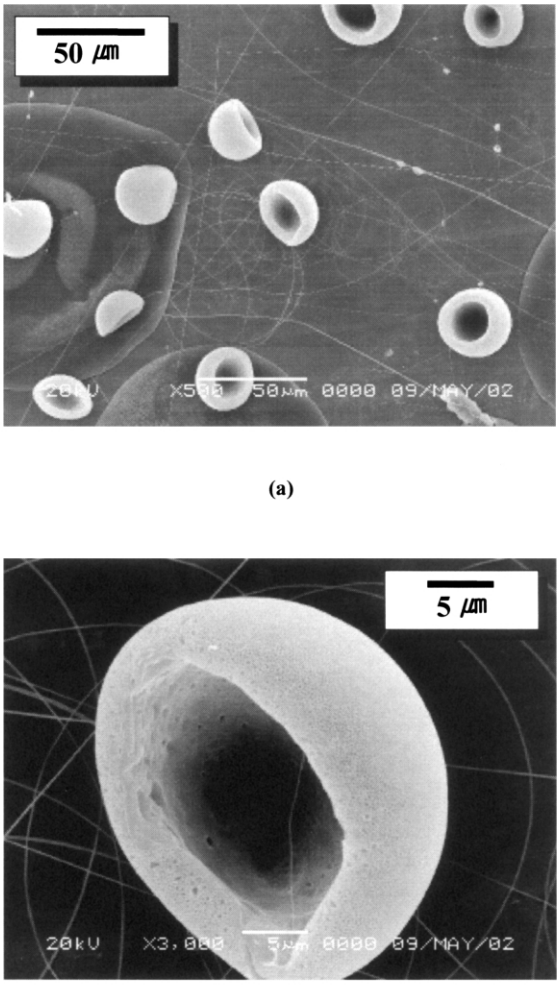


(a)

(b)

(c)

Fig. 4. SEM photographs of PS fibers produced from the mixed solvent with THF/DMF (v/v) ratios of (a) 100/0, (b) 50/50, (c) 0/100. The solution concentration, applied voltage, and TCD were 13 wt%, 15 kV, 12 cm, respectively.



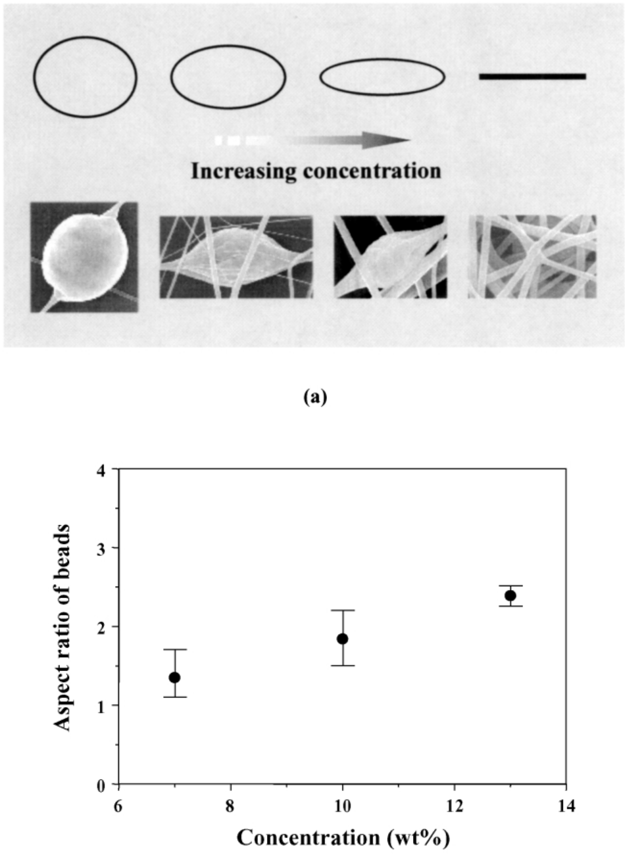
(a)

(b)

Fig. 5. SEM photographs of a significant feature like HHS, (a) × 500, (b) × 3000.

interaction in polymer-solvent system (binary system) is either attractive or repulsive which depends on the type of solvent [22]. The intermolecular interaction in binary system can be either repulsive or attractive, depending on the solvent used. Therefore, viscosity has a large affect in electrospinning. Fig. 3 shows the viscosity of PS solution increasing with higher DMF content. It is noted that PS solutions under investigation had viscosities ranges between 42–48 centipoise (cPs).

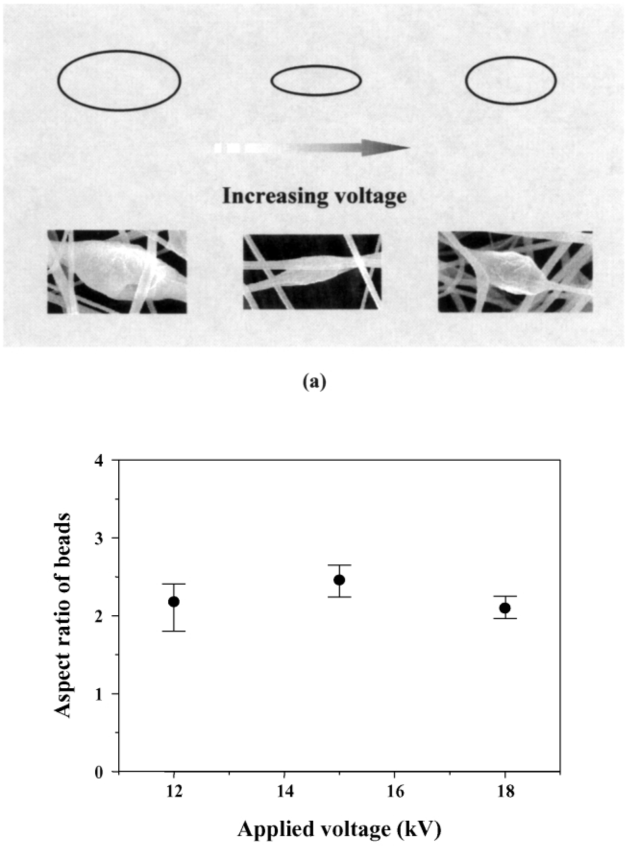
Fig. 4 exhibits SEM photographs of electrospun PS fiber prepared from THF/DMF solvents in ratios of 100/0, 50/50 and 0/100 (v/v). In case of PS dissolved only in THF, the capillary tip often became blocked due to the low boiling point of the solvent. Also, owing to the low dielectric constant (7.3) of the THF solvent, electrospinning was nowhere to be facilitated [23]. Under SEM examination showed a significant feature like what appears to be like structure half hollow sphere (HHS), as indicted in Figs. 4(a) and 5. It had a diameter between 20–30 μm, which was



(a)

(b)

Fig. 6. (a) The change of bead morphology and (b) the aspect ratio with the polymer concentration (PS dissolved in the mixture of THF/DMF, 50/50 (v/v)). The applied voltage and TCD were 15 kV, 12 cm, respectively.



(a)

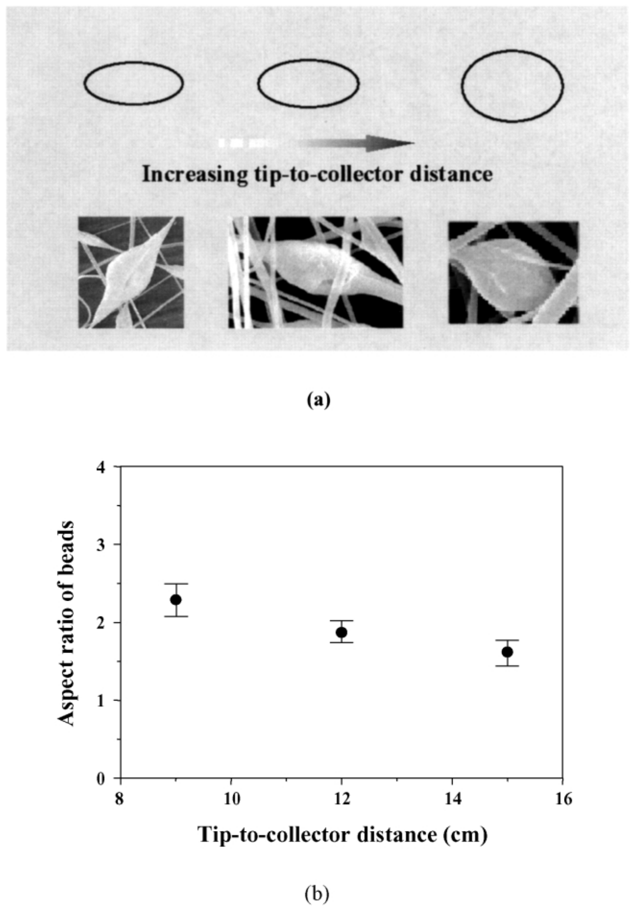
(b)

Fig. 7. (a) The change of bead morphology and (b) the aspect ratio with the applied voltage (PS dissolved in the mixture of THF/DMF, 50/50 (v/v)). The solution concentration and TCD were 13 wt%, 12 cm, respectively.

quite different than the usual beads. While beads were mainly formed along the electrospun fibers, HHS was irregular and independent in terms of location of formation. The production of HHS may be due to the combined effects of polymer, solvent and electric force applied. Since THF is known to readily absorb oxygen in air, and since the process of electrospinning is done in air, this may be the reason for the HHS formation. Fong [24] reported that the formation of ribbon shaped fibers was caused by the rate of solvent evaporation. Bognitzki [25] and Caruso [26] on the other hand reported that porous structure on the electrospun fiber was related to the use of volatile solvents and rapid phase separation during the electrospinning process. However, since authors did not give any details of the mechanisms to explain these unexpected experimental results, a further investigation should provide useful. The electrospinning from PS in THF produced a structure having a combination of fibers, beads and HHS. Furthermore, the addition of DMF enhanced the electrospinning in addition to eliminating structures other than the fibers. The latter may be a result of high dielectric constant (36.7 at 25 °C) and electrolyte behavior of DMF [27], where DMF is randomly dissociated into positive and negative charges in solution [28].

Solution concentration is one of the important parameters in electrospinning. To prepare fibers by electrospinning, proper polymer concentration and viscosity are required. If polymer concentration is too low, fibers are not formed but only droplets are produced due to the jet breaks up into droplets known as the electrospray. Electrospinning is suppressed at too high polymer concentrations because it prohibits flow of a polymer solution continuously to the capillary tip. Thus in some range of polymer concentrations, where solution viscosity is proper, electrospinning achieved while in lower and upper ranges of concentrations, electrospary and suppression dominantly occurs. As discussed above, fabrication and the resulting fiber morphology development are dependent on solution viscosity. For the electrospun fibers produced with below 15 wt% solutions of PS, bead structures were observed. The morphology of beads and fibers was changed by polymer concentration, applied voltage and TCD.

Fig. 6(a) illustrates, the change of bead morphology with



(a)

(b)

Fig. 8. (a) The change of bead morphology and (b) the aspect ratio with the TCD (PS dissolved in the mixture of THF/DMF, 50/50 (v/v)). The solution concentration and applied voltage were 13 wt%, 15 kV, respectively.

polymer concentration (PS dissolved in the mixture of THF and DMF, 50/50 by volume). The aspect ratio of the bead is seen to change with polymer concentration. At least 5–10 beads were measured for the aspect ratio (major axis: bead length along the fibers/minor axis: bead length perpendicular to the fiber). The aspect ratio increased continuously with increasing polymer concentration (Fig. 6(b)). At lower than 15 wt% concentration, bead structures formed, as viscosities were low and thus making the jet formation unstable. At above 15 wt% concentration, only fibers were formed due to high viscosity (Fig. 6(a)).

The shape of the droplet at the syringe tip can be changed by the intensity of the applied voltage and the resulting beads morphology and aspect ratio were changed accordingly (Fig. 7(a)). Overall, the aspect ratio increases first and then decreases with the applied voltage, with this transition occurring at 15 kV (Fig. 7(b)). The increase (0–15 kV) may be due to increasing applied voltage giving rise to higher electrostatic repulsion force between capillary tip and collector which in turn provides higher drawing stress in the jet, hence making the bead size smaller. At above 15 kV, in which the aspect ratio decreases, no explanation is available at this time. However, Deitzel [14] reported that the bead defect density increased with increasing voltage in PEO/water systems.

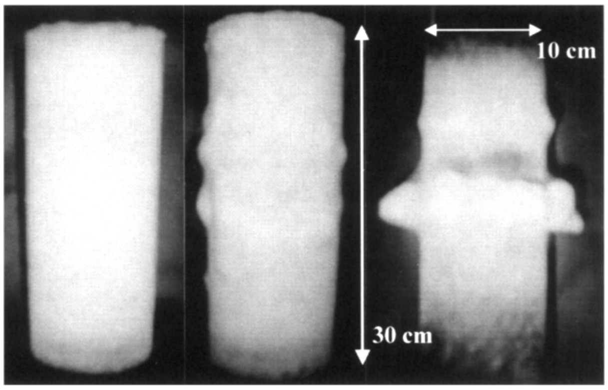


Fig. 9. The different appearance of PS non-woven mats.

The change of beads morphology and the aspect ratio with TCD is shown in Fig. 8. With increasing TCD, minor axis of the bead became larger. When the applied voltage is constant, the electrostatic force will be decrease as TCD increases. As a result, drawing stress on the jet decreases. The aspect ratio decreased slowly with TCD (Fig. 8(b)).

Fig. 9 shows that different appearance of PS non-woven mats prepared. It prepared as controlling electrospinning parameters. The relation between the throughput and the electric conductivity is shown in Fig. 10. The throughput increased gradually with increasing electric conductivity of PS solution, which meant that the throughput was closely related with electric conductivity.

4. Conclusions

The electrospun PS fibers have been successfully prepared by using different concentration of PS solutions. The morphology of the formed beads was strongly affected by the parameters such as polymer concentration, applied voltage, and TCD. At below 15 wt% polymer solutions,

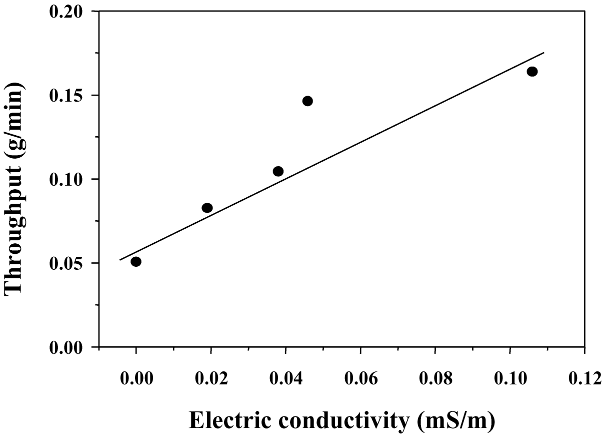


Fig. 10. Plot of the throughput versus the electric conductivity.

electrospinning was not enhanced due to the low viscosity. The fibers formed were without beads at polymer concentration higher than 15 wt%. For these concentrations, electrospinning dramatically improved and the average fiber diameter was hardly affected when DMF was added. The HHS structure was observed when the PS was only dissolved THF. The surface tension and electric conductivity of polymer solution were strongly correlated to the critical voltage and throughput, respectively.

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