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Patterned Polydiacetylene-Embedded Polystyrene Nanofibers Based on Electrohydrodynamic Jet Printing

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Abstract: Electrohydrodynamic (EHD) jet printing is a direct-writing technique which ejects ink through a fine nozzle using an electric field, which has the advantages of high-resolution, rapid printing speed and a wide range of ink selectivity. In this article, the EHD jet printing system is utilized to print patterns of polystyrene (PS) nanofibers. The effect of parameters such as ink concentration, working distance, applied voltage, and stage speed on the diameter of the printed nanofibers was investigated. The EHD jet printing technology is further utilized to print various patterns of polydiacetylene (PDA)-embedded PS nanofibers. The EHD jet printing based nanofiber printing is advantageous over conventional electrospining based approaches in terms of patterned PDA images. In addition, an advanced EHD jet printing system which is adopted for aligned nanofiber printing will expand the application of nanofibers from bio and chemical sensors to tissue engineering and electronics.

Keywords: electrohydrodynamic jet printing, nanofiber patterning, electrospinning, polydiacetylene, polystyrene.

Introduction

The electrospinning technique, which uses an electric field to draw fine fibers from the nozzle, is a widely used nanostructure fabrication method.[1-9] When a sufficiently high voltage is supplied to the solution, repulsive charges form in a solution droplet and counteract the surface tension. At a critical point, when the electrostatic repulsion overcomes the surface tension, a liquid jet erupts from the droplet. The jet is stable near the edge of the nozzle but it becomes unstable and elongated by the whipping process due to bending instability. The whipping process in the electrospinning system leads to the formation of uniform fibers with micrometer- to nanometer-scale diameters. Because of the bending instability in the electrospinning system, however, the electrospun fibers are always collected in the form of intricate and random webs or mats. The difficulty of accurate positioning and aligning of electrospun nanofibers limits their applications; thus, it is crucial to align the electrospun nanofibers. Typically, two methods have been used in an attempt to align the electrospun nanofibers. First, the electrospun nanofibers can be aligned by collecting the nanofibers with a spinning wheel-type collector.[10-13] The nanofibers are collected on the edge of the spinning wheel, which leads to an aligned nanofiber deposition. Second, aligned nanofibers can be deposited by collecting them with parallel electrodes. During the deposition, the electrospun nanofibers deflect between the parallel electrodes, which results in an alignment of the electrospun nanofibers across the electrodes.[14-17] However, these methods still lack control, positioning and degree of alignment capability.

Electrohydrodynamic (EHD) jet printing systems, which are comprised of a print head with a fine nozzle, pneumatic regulator, mobile stage and high-voltage power supply, eject the ink through a fine nozzle tip using an electric field, similar to the electrospinning method.[18] The EHD jet printing technique, due to the jetting principle, has advantages such as high-resolution and broad ink selectivity compared to conventional ink jet printing methods. It can print patterns as small as a few hundred nanometers with various inks such as protein, DNA, carbon nanotube, polyurethane and block copolymer.[19-22] The EHD jet printing system is similar to an electrospinning system except for the distance between the nozzle and the collector. In a conventional electrospinning system, the nozzle is placed over 10 cm from the target. On the contrary, for EHD jet printing, the distance is in the range of hundreds or

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tens of micrometers. Due to the short distance between the nozzle and collector in EHD jet printing, positioning, aligning and direct-writing of nanofiber patterns on the collector is more accurate than with electrospinning, which collects nanofibers into a random web or mat by whipping through relatively long distances. Recently, Lee *et al*. reported an EHD nanowire printing method and demonstrated the fabrication of field effect transistors.[23-25]

Polydiacetylenes (PDAs) are structurally very unique conjugated polymers.[26-28] Unlike other conjugated polymers, PDAs are prepared by polymerization of self-assembled diacetylene (DA) monomers. Thus, PDAs are intrinsically supramolecular aggregates and generally have an absorption maximum at around 650 nm that corresponds to a blue color owing to the extensive and efficient overlap of p-orbitals. PDAs often display a distinct blue-to-red color change in response to diverse environmental stimuli including physical (heat, mechanical strain, magnetic field, electric current, *etc*.) and chemical/biochemical (solvent, ions, specific ligand-receptor interactions, *etc*.) inputs.[29-36] In addition, the stress-induced colorimetric transition is accompanied by generation of red fluorescence.[37,38] Accordingly, both colorimetric and fluorogenic properties of PDA has been actively employed as output signals in a variety of PDA based sensor systems.[29-38]

Recently, a conceptually new strategy was introduced to PDA sensors. Electrospinning of a viscose solution containing matrix polymers and diacetylene monomers allowed fabrication of PDA nanofibers after UV-induced polymerization.[39] The electrospun PDA mat was found to be suitable for selective[40] and sensitive[41] detection of target molecules. Owing to the intrinsic difficulty, well aligned PDA-embedded nanofibers from the conventional electrospinning methods have been almost impossible. Herein, we report, as part of our continuing efforts for the development of patterned PDAs, micropatterning of PDA-embedded polymers by employing the EHD technique. Various shapes of PDA-embedded polystyrene nanofiber patterns are printed on Si substrates by combining the bottom-up method of self-assembly of DA monomers with a top-down method of EHD jet printing. This methodology also enables accurate positioning and registration of nanofibers with different compositions on a substrate. The printed patterns of PDA-embedded PS nanofibers exhibit a typical blue-to-red color transition and emit a red fluorescence after the substrate is heated at 80 ºC for 1 min. In addition, the effect of concentration of ink, working distance and applied voltage on the diameter of the printed polymers was probed with polystyrene nanofibers.

Experimental

Preparation of Inks for EHD Jet Printing. Polystyrene (PS) inks were prepared by dissolving 1 to 5 wt% PS (Polymer Source) in 1,2,4-trichlorobenzene (Sigma Aldrich). A diacetylene monomer, 10,12-pentacosadiynoic acid (PCDA) (Sigma Aldrich) was dissolved in 5 g of 1,2,4-trichlorobenzene (Sigma Aldrich), and the organic solution was filtered through a 1 μm filter. 0.15 g of PS was added into 4.85 g of filtered PCDA solution.

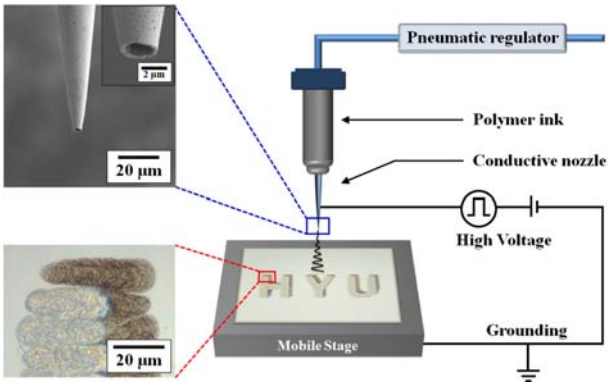

Figure 1. Schematic of electrohydrodynamic jet printing system.

Preparation of Nanofiber Printing Set-Up. Figure 1 shows a schematic of an EHD jet printing system which is used for nanofiber printing. The system is comprised of a print head, pneumatic regulator, mobile stage and high-voltage power supply which are connected and controlled electronically. The glass capillary nozzles (inner diameter of 2 μm and outer diameter of 2.66 μm, World Precision Instruments) were coated with an Au/Pd (15 nm) layer for conductivity using a sputter coater (Denton, Desk II TSC), and the nozzle was immersed into 0.01 wt% 1H,1H,2H,2H-perfluorodecane-1-thiol solution in DMF to form a hydrophobic coating on the nozzle. The ink was injected into the nozzle tip using compressed air, and then the pressure of the pneumatic regulator was maintained at 0 psi.

EHD Jet Printing Conditions for Nanofiber Deposition. 1 to 5 wt% PS inks were used to observe the effect of ink concentration on the formation of nanofibers and nanofiber patterns. To investigate the effect of operating factors such as working distance, applied voltage, and stage speed, the working distance was tested at 20, 30, and 40 μm, the applied voltages were varied from 500 to 400 V in 25 V decrements and stage speed was varied from 0.01 to 10 mm/s. For PDA-embedded PS nanofiber pattern printing, the system was operated at a working distance of 30 μm, applied voltage of 450 V, and 0.2 mm/s stage speed. The computer program was used to print various pattern shapes.

Characterization. For morphological analysis of the patterns, scanning electron microscopy (SEM) was performed with a Hitach S-4800, and optical and fluorescent images were acquired with a Nikon ECLIPSE LV100D microscope equipped with a mercury arc lamp.

Results and Discussion

Initial phase of current investigation focused on the effect of several key parameters on the diameter of the nanofibers since it is related to the sensitivity and permeability of the

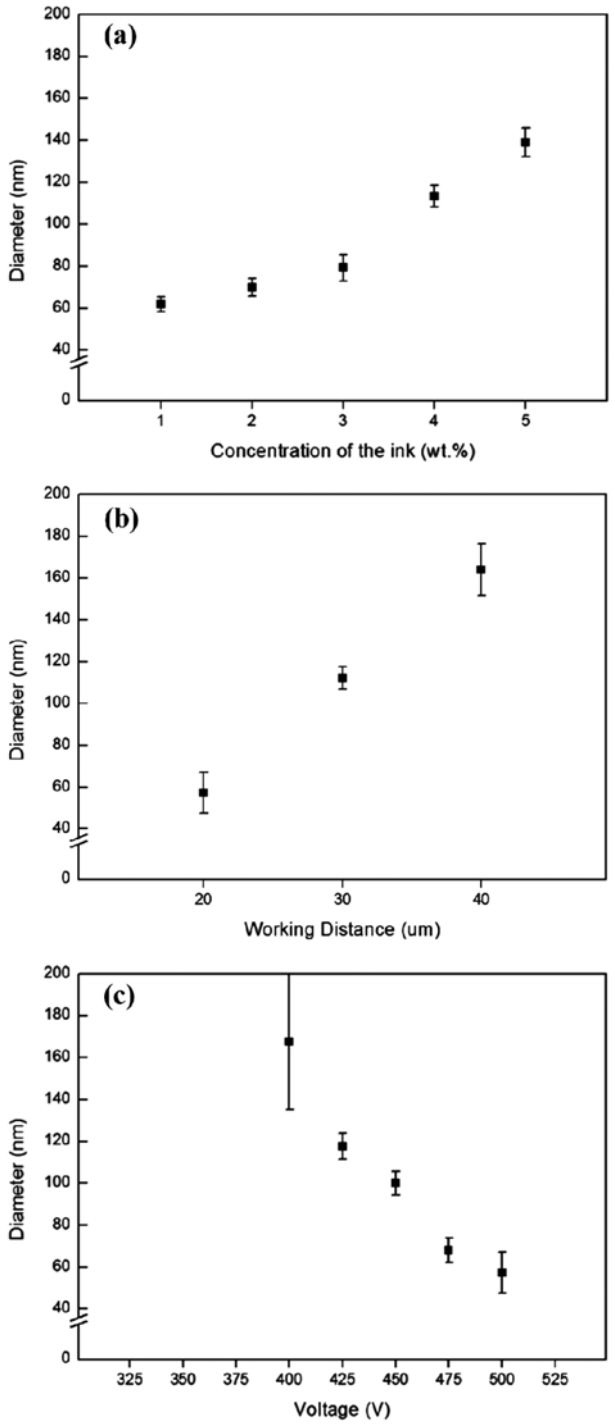

Figure 2. The diameter of PS fibers as a function of (a) concentration of ink, (b) working distance and (c) applied voltage.

polymer fibers. Key parameters controlling the diameter of the nanofibers produced by electrospinning are concentration of polymer solution, working distance, and applied voltage. In order to investigate those parameters, polystyrene (PS) nanofibers were prepared by the EHD jet printing method under different fabrication conditions. Figure 2 shows the results of our investigation obtained by changing ink concentration, working distance and applied voltage. To understand diameter variation of the nanofiber with the concentration of inks, a series of experiments are carried out in which the concentration of inks is increased from 1 to 5 wt% in 1 wt% increments, with constant applied voltage and working distance at 475 V and 30 μm, respectively. The diameters of printed nanofibers are 61.74±3.59 nm, 69.93±4.29 nm, 79.31±6.27 nm, 113.30±5.25 nm, and 138.99±6.74 nm, respectively, from 1 to 5 wt%. The diameter of the nanofiber increases with ink concentration which is associated with the viscosity of the ink. This result is consistent with that for conventional electrospinning method.[3-8] In order to understand diameter variation of the nanofiber with the applied voltage, the fiber is printed at a working distance of 20 μm using 5 wt% ink, and the applied voltage is decreased from 500 to 400 V in 25 V decrements. The diameters of the nanofiber from 500 to 400 V are 57.32±9.82 nm, 68.11±5.79 nm, 99.99±5.67 nm, 117.68±6.18 nm, and 167.49± 32.32 nm, respectively. The diameters of the nanofibers are increased with decreasing applied voltage. With decreasing the applied voltage, the electric field is also decreased, so it will decrease the electrostatic repulsive force on the fluid jet which favors the thicker fiber formation.

To observe diameter variation with working distance, nanofiber printing is carried out at an applied voltage of 500 V, and working distances of 20, 30, and 40 μm. The diameters of the nanofibers are observed to be 57.32±9.82 nm, 112.20 ±5.33 nm, 163.99±12.35 nm at 20, 30, and 40 μm, respectively. Various effects may contribute to fiber-diameter variation as the working distance changes. Generally, as the working distance increases, the elongational process induced by bending instability and the evaporation of solvent are enhanced, which results in a decrease in fiber diameter. However, as the working distance increases, the electric field decreases resulting in an increase in fiber diameter. In this system, the change in working distance may not affect the elongational process and solvent evaporation because the working distances are very short from 20 to 40 μm and a non-volatile solvent, 1,2,4-trichlorobenzene, is used in the solution. Thus, the electric field is dominant in determining the fiber diameter.

Stage speed is one of the important process parameters that affect the shape of the nanofibers deposited by using the EHD jet printing system. To observe shape variation in the deposited individual nanofibers with stage speed, the fiber is printed with 2 wt% PS ink at an applied voltage and working distance of 475 V and 20 μm, respectively, and stage speeds are increased from 0.01 to 2 mm/s. The SEM image in Figure 3(a) shows shape variation in the deposited individual nanofibers with stage speed. When the charged nanofiber is deposited on the silicon substrate, residual charges on the substrate could affect the deposition behavior. When the stage speed is much smaller than the deposition rate, the nanofiber is affected by the repulsive force from the residual charges and

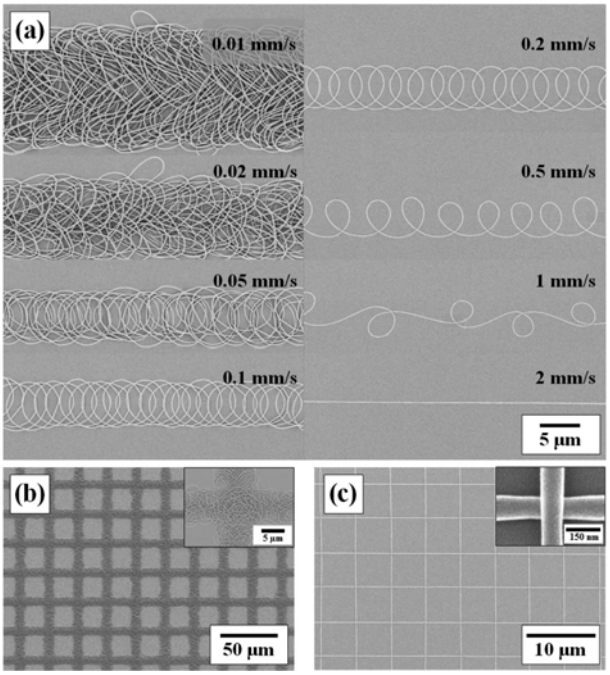

Figure 3. (a) The shape variation of PS nanofibers patterns with the stage speed. Grid patterns composed with (b) nonwoven lines and (c) individual PS nanofibers. The grid patterns with nonwoven lines and single nanofiber are printed at 0.02 and 2 mm/s, respectively.

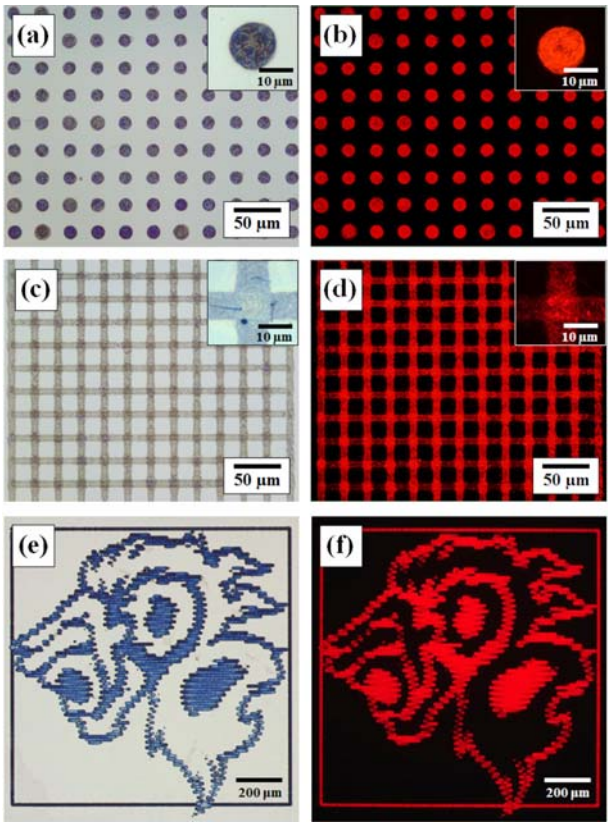

Figure 4. Optical ((a), (c), (e)) and fluorescence ((b), (d), (f)) images of dot, grid and the logo of the university composed with PDA-embedded PS nanofibers. The fluorescence images are obtained by heating the fibers at 80 ºC for 1 min.

resulted in oscillation or buckling motions. However, when the stage speed is larger than the deposition rate, a straight-line nanofiber can be obtained. As summarized in the Figure 3(a), ~15 μm wide nonwoven line pattern is printed at the stage speed of 0.01 mm/s. As the stage speed is increased, the width of the nonwoven line pattern and density of the nanofiber are decreased due to a decrease in the amount of fiber deposits per unit area. When the stage speed reaches to 0.1 mm/s, a nanofiber with a coiled shape is deposited in a narrower zone. With further increasing of the stage speed, a nanofiber with less number of loops is deposited, and a straight-line nanofiber is obtained at the stage speed of 2 mm/s. By using the variation in pattern form, we have printed two grid patterns composed with nonwoven lines and individual nanofibers which are shown in Figure 3(b) and (c), respectively.

Compared to the stage speed of 2 mm/s for straight-line patterning, the previous reports on use of electrospinning have required faster stage speed (20-1500 mm/s).[42-46] Note that slow stage speed is an advantage to acquiring highly precise position and alignment of nanofibers. In order to investigate the feasibility of EHD jet printing method for aligned PDA nanofibers, DA-embedded PS nanofibers were fabricated. It is expected that UV induced polymerization of DA embedded PS fibers should results in the generation of PDA supramolecules in the fibers. In our earlier studies,[39] we have observed efficient formation of PDAs in the electrospun polymer fibers by 254 nm UV irradiation. Figure 4 shows optical and fluorescent microscope images of several different patterns of PDA-embedded PS nanofibers fabricated on Si substrates. Diacetylene monomers embedded in the printed PS nanofiber are easily polymerized by irradiating with 254 nm UV light (1 mW/cm^2) for 1 min (Figure 4(a), (c), and (e)). The appearance of a blue color is a strong indicative of PDA formation. Furthermore, it has been well known that the blue phase PDAs are nonfluorescent while the red phase counterparts are fluorescent.[37,38] Thus, if the heat treated PDA embedded PS fibers emit red fluorescence, it would be another critical evidence of successful generation of PDAs in the nanofibers. To test this, the UV treated patterned PS nanofibers were subjected to heating (80 ºC, 1 min). As displayed in Figure 4(b), (d), and (f), the red fluorescence is observed from the printed nanofiber patterns after the heat treatment. Capability to achieve accurate registration of nanofibers with different compositions is demonstrated in Figure 5. The printed letters are composed with pure PS and PDA-embedded PS nanofibers. The brighter parts correspond to pure PS nanofibers and the darker parts consist of PDA-embedded PS nanofibers. As shown in Figure 5, the optical and fluorescence micro-

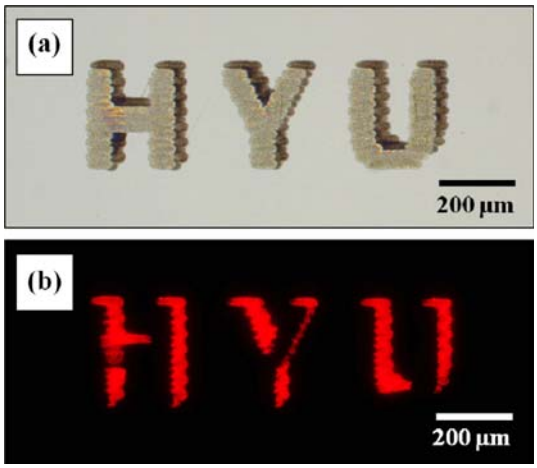

Figure 5. Optical (a) and fluorescence (b) images of the initial letters of the university composed with PS and PDA-embedded PS nanofibers (shaded areas in the optical images). The fluorescence images are obtained by heating the fibers at 80 ºC for 1 min.

scope images display successful printing of the thoroughly registered nanofiber patterns with different compositions.

The patterned PDA-embedded fibers displayed in Figures 4 and 5 demonstrate the efficiency of the EHD jet printing method. These micron-sized arrays or patterns of PDA-embedded nanofibers could not be achieved by conventional electrospinning methods.[39-41] It should be noted that current investigation focused on the fabrication rather than the application of the PDA-embedded polymer nanofibers using the EHD jet printing method. The simple and straightforward method should allow fabrication of diverse PDA-encapsulated patterned nanofibers for colorimetric sensor applications.

Conclusions

In this research, we have successfully fabricated micron-sized patterns of PS and PDA-embedded PS nanofibers on a silicon substrate by using a direct-writing method *via* EHD jet printing. The diameter of the nanofiber increases with increasing ink concentration and decreasing applied voltage, which is similar to the conventional electrospinning method. However, the diameter variation with the working distance contrasted with conventional electrospinning due to the short working distance of 20 to 40 μm in the EHD jet printing system. We have also showed a blue-to-red color transition and generation of red fluorescence from the photo-synthesized PDA-embedded PS nanofiber patterns upon heat-treatment. The utilization of EHD jet printing technology for aligning nanofibers and patterning nonwoven nanofibers will expand the applications of fibrous polymers.

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