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Spontaneous Formation of Poly(*p*-phenylenevinylene) Nanofiber Yarns through Electrospinning of a Precursor

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Poly(*p*-phenylenevinylene) (PPV) has been paid considerable attention due to its properties of electrical conductivity, electro- or photoluminescence, and nonlinear optical response, which have potential applications in electrical and optical devices, such as light-emitting diodes,[1] solar cells,[2] and field-effect transistors.[3] Most of the work with regard to PPV exploits thin coatings or cast films,[4] while a few reports have been investigated on PPV nanofibers by chemical vapor deposition polymerization with nanoporous templates.[5] The electrospinning, a simple, rapid, inexpensive, and template-free method, capable of producing submicron to nanometer scale fibers is applied to fabricate nanofibers of conducting polymers, such as sulfuric acid-doped polyaniline[6] or a blend of camphorsulfonic acid-doped polyaniline and poly(ethylene oxide).[7] However, the electrospinning is not applicable to PPV because of its insoluble and infusible nature. Although poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene], an electroluminescent derivative of PPV, could be electrospun from 1,2-dichloroethane solution as a randomly oriented mesh, the resulting fibers were not uniform exhibiting leaflike or ribbonlike morphology due to the low viscosity limited by the polymer solubility.[8] This short Communication deals with a study on fabrication of centimeters-long PPV nanofiber yarns by electrospinning of a soluble precursor and subsequent thermal conversion. The effect of spinning conditions on morphology and structure of the resulting nanofiber yarns has been briefly investigated.

Poly(*p*-xylenetetrahydrothiophenium chloride), a precursor of PPV, was commercially available in the form of 0.25% aqueous solution from Aldrich Inc. The $\bar{M}_w$ determined by membrane osmometry was 1.3×10^5, while low-angle laser-light scattering combined with centrifugation yielded $\bar{M}_w = 9.9 \times 10^5$ ($\bar{M}_n = 5.0 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.0$).[9] About 1 mL of a precursor solution containing different amount of methanol was poured into a glass syringe (12 mm in diameter), and an electric field was applied to a single-hole spinneret (340 μm in diameter) from a variable high-voltage power supply (Towa Keisoku Inc.) capable of applying positive voltages (E) up to 30 kV. The electrospun fibers were collected on a grounded flat plate (10 × 10 cm) covered with an aluminum foil used as a target where the distance between the needle and the target electrode was 20 cm. The viscosity of the precursor solution was measured at 30 °C with a B-type viscometer (VM-10A, CBC Materials Inc.).

Unlike electrospun fibers directly deposited on the grounded target as a randomly oriented mesh, centimeters-long precursor fibers are spontaneously electrospun into yarns vertically on the surface of the aluminum target parallel to the electric field within a minute (Figure 1). The unusual formation of precursor yarns can be explained by the conducting nature of the precursor: the deposited precursor fibers discharge through polyelectrolyte chains to the grounded target, which prefers the following deposition on the fibers so as to decrease the gap between the fibers and the needle. Once a yarn is formed by touching the adjacent fibers swinging under the instable jet, the following deposition may occur preferably on the yarn rather than on the individual fibers because of the low resistance. An electrostatic attractive force stretches the yarn vertically on the target electrode, leading to a successive upward growth of the yarn. Although the precursor is partially converted to semiconducting PPV,[4] the discharge may occur through ionic conduction. Indeed, a rise in the ambient humidity from 50 to 70% RH results in a rapid growth of the yarn and increases the electric current from 1.7 to 2.6 μA at $E = 20$ kV. On the other hand, the current is less dependent on the humidity in the absence of the precursor polymer (0.39−0.46 μA at $E = 20$ kV). Furthermore, a similar phenomenon is observed for other ionic conducting polyelectrolyte such as poly(acrylic acid).

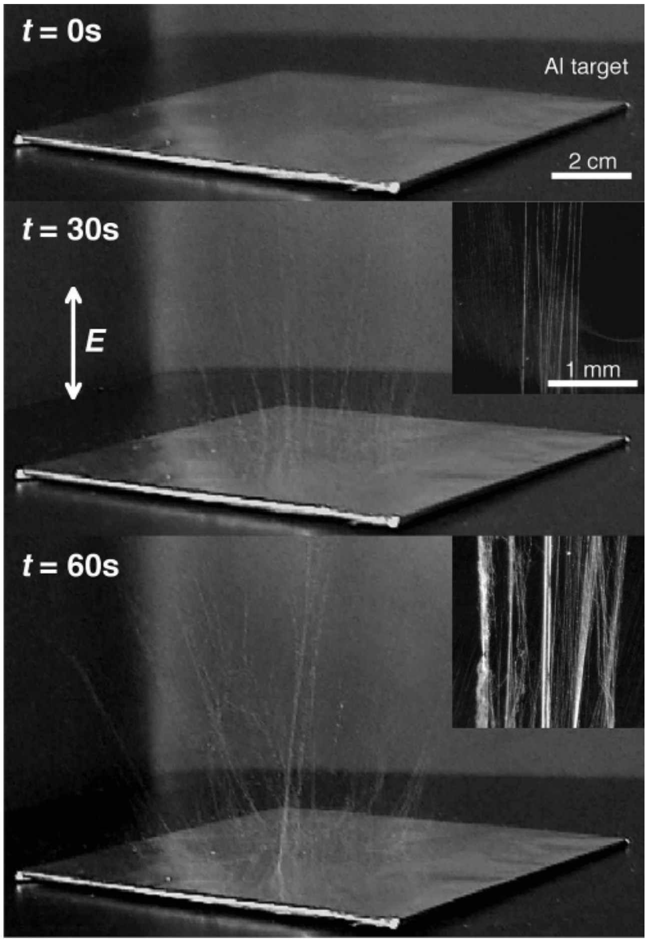

Figure 1. Spontaneous formation of precursor yarns by electrospinning of a precursor solution with methanol content (C_{MeOH}) of 60% at $E = 20$ kV for 0, 30, and 60 s.

It is seen from Figure 2 that at $E = 20$ kV the precursor yarn is formed in a range of methanol content (C_{MeOH}) between 40% and 90%, corresponding to the concentration of precursor ($C_{\mathrm{precursor}}$) between 0.15% and 0.025%, while at $C_{\mathrm{MeOH}} < 40\%$ ($C_{\mathrm{precursor}} > 0.15\%$) no yarn is formed at E up to 30 kV as the viscosity of the solution ($\eta > 8.8$ cP) is too high to maintain a

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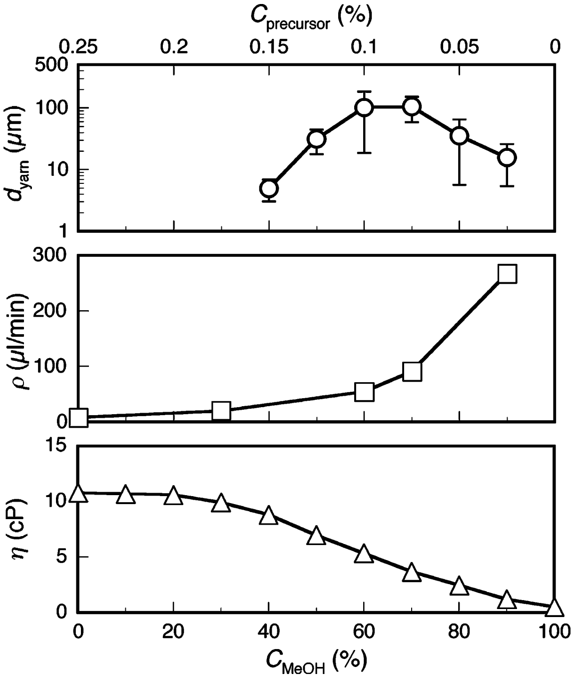

Figure 2. Dependence of methanol content (C_{MeOH}) and concentration of precursor ($C_{\text{precursor}}$) on average diameter of precursor yarn (d_{yarn}) and average spinning rate (ρ) at $E = 20$ kV for 10 min and viscosity of the solution (η) measured at 30 °C with a B-type viscometer.

continuous jet from the spinneret. On the other hand, at $C_{\text{MeOH}} > 90\%$ ($C_{\text{precursor}} < 0.025\%$), small droplets of the solution are collected on the surface of the aluminum target, which is ascribed to the low viscosity ($\eta < 1.2$ cP) and surface tension not enough to maintain a stable drop at the spinneret. Here, methanol is crucial to increase the volatility of solvent as well as to decrease the surface tension, which arises from the fact that dilution with pure water never yields yarn. The average diameter of the yarn (d_{yarn}) electrospun at $E = 20$ kV for 10 min, representing a growth rate of the yarn, increases from 5 to 100 μm as C_{MeOH} rises from 40% to 70%. This can be explained by the increase of spinning rate (ρ), defined as the average volume of the solution electrospun in 1 min, due to the decrease of the value of η. A further increase of C_{MeOH}, however, yields finer yarns owing to the decrease of $C_{\text{precursor}}$.

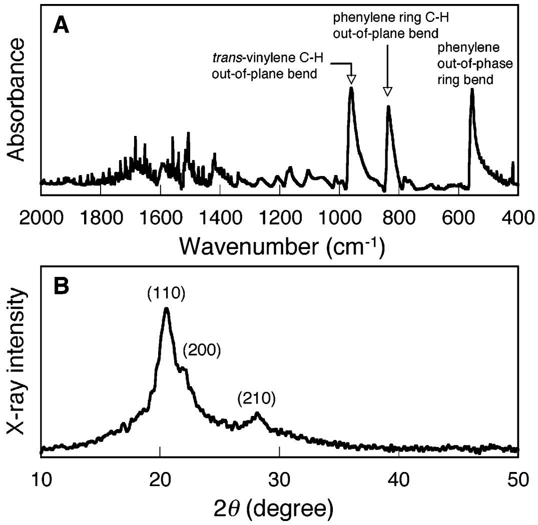

Figure 3. (A) FT-IR spectrum and (B) wide-angle X-ray diffraction pattern of PPV nanofiber yarns.

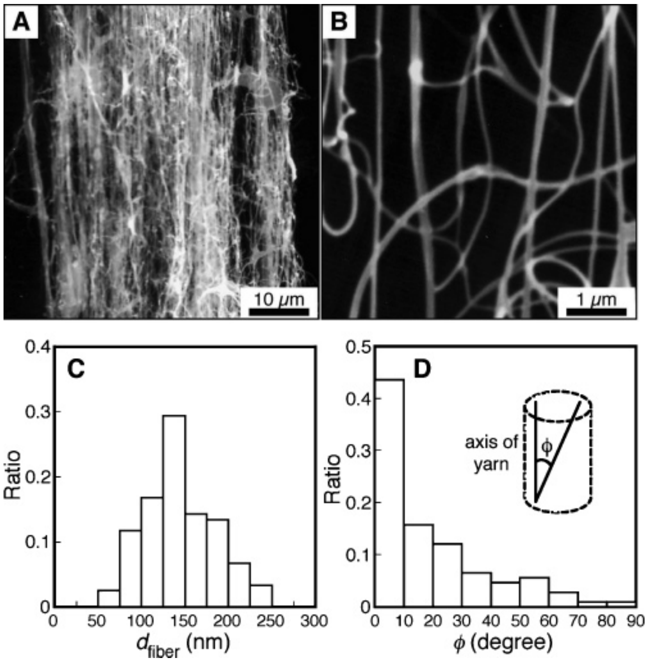

Figure 4. (A, B) SEM images of PPV nanofiber yarn, (C) distribution of diameter (d_{fiber}), and (D) orientation of PPV fibers along the axis of the yarn fabricated by thermal conversion (250 °C for 12 h in a vacuum) of the precursor yarn ($C_{\text{MeOH}} = 60\%$, $E = 20$ kV for 10 min).

The precursor yarns are subsequently converted to PPV yarns by heat treatment at 250 °C for 12 h in a vacuum. About 44% weight loss of the as-electrospun precursor yarns in a temperature range of 25−300 °C, corresponding to the elimination of moisture, tetrahydrothiophene, and hydrochloric acid, decreases to less than 0.01% after the heat treatment, demonstrating that the precursor unit is completely converted to PPV. The FT-IR spectrum of the resulting PPV yarns measured with a FTIR-8100 (Shimadzu Inc.) shows a clear peak at 965 cm^{-1} corresponding to the *trans*-vinylene C−H out-of-plane bend but no absorption at 632 cm^{-1} to the C−S stretch of the precursor (Figure 3A). A clear indication of paracrystalline structure is seen in a wide-angle X-ray diffraction pattern measured with a RINT (Rigaku Inc.), as shown in Figure 3B. The PPV yarns show clear peaks at $2\theta = 20.5°$ ($d = 4.33$ Å) and 28.2° ($d = 3.16$ Å) and a shoulder at $2\theta = 22.0°$ ($d = 4.03$ Å), corresponding to the diffractions from (110), (210), and (200) planes of the monoclinic unit cell of the PPV crystal,[10] respectively. Since the as-spun precursor fibers are amorphous, the crystallization will take place during the heat treatment. The degree of crystallinity estimated from the WAXD pattern is 45%, and the apparent crystallite size normal to the (210) plane calculated from Scherrer's equation is 75 Å. The diffraction patterns of the side and end views of the PPV yarns are substantially the same, indicating no notable orientation of PPV chains on a molecular level.

It is seen from Figure 4A,B that the fibers preserve their morphology even after the elimination reaction with an average diameter (d_{fiber}) of 150 nm, and more than 25% of fibers are finer than 100 nm (Figure 4C). We should emphasize here that the PPV fibers are uniaxially aligned along the axis of the yarn where about 70% of the fibers have a tilt angle (ϕ) within 30° (Figure 4D). This can be explained by the electrostatic repulsion between positively charged fibers deposited on the yarn[11] and/or by stretching the fibers due to the electrostatic attractive force between the needle and the yarn in favor of discharging through the yarn, leading to a configuration in parallel alignment. A preliminary experiment of doping with sulfuric acid results in a color change from brown to black with certain resistance, and

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a detailed study on electrical conductivity of individual fibers is currently underway. Furthermore, uniaxially aligned carbon nanofiber yarns can be conveniently produced via carbonization of PPV.

Thus, the bottom-up formation of semiconducting or conducting nanofiber yarns is of importance not only from the fundamental viewpoints for understanding the intrinsic electrical and mechanical properties in a nanoscale but also from the practical use for electromagnetic interference shielding or conducting textiles, which is expected to open up a new field of applications in organic nanoelectronics.

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