Electrostatically-generated nanofibers of electronic polymers

A.G. MacDiarmid[a*], W.E. Jones, Jr.[a], I.D. Norris[a], J. Gao[a], A.T. Johnson, Jr.[b], N.J. Pinto[a],
J. Hone[b], B. Han[c], F.K. Ko[c], H. Okuzaki[a], M. Llaguno[b]

[a] Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323 USA
[b] Department of Physics, University of Pennsylvania, Philadelphia, PA 19104-6323 USA
[c] Fibrous Materials Research Center, Drexel University, Philadelphia, PA 19104 USA

Abstract

Long nanofibers of conducting electronic polymers and their blends and also conventional polymers are conveniently fabricated in air by a non-mechanical electrostatic dispersion method. All fibers in a given preparation of certain polymers have diameters < 100nm. Fibers of 100% doped polyaniline as well as its blends in polymers such as polystyrene and polyethylene oxide have been prepared. Current/voltage in addition to conductivity/temperature relationships of single fibers as small as 419 nm have been obtained. Polyacrylonitrile and polystyrene fibers can be easily and uniformly coated from aqueous solution with conducting polypyrrole or with gold by electroless deposition. Polyacrylonitrile fibers can be thermally converted to conducting carbon nanofibers.

Keywords: Solution processing, Scanning electron microscopy, Coatings, Polyaniline and derivatives, Polypyrrole and derivatives

1. Introduction

It is commonly accepted that the rapidly-expanding field of nano-materials is defined as one consisting of a substance or structure which exhibits at least one dimension of less than 100 nm (0.1 μm).[†] [1]

The objectives of the present study were: (i) to develop a method by which nanofibers (diameter < 100 nm) of organic polymers could be controllably and reproducibly fabricated such that in one given preparation, all fibers would have a diameter < 100 nm and (ii) to reproducibly and controllably fabricate, for the first time, nanofibers of pure electronic polymers (in their semiconducting and metallic regimes) and/or their blends in conventional organic polymers for the purpose of ascertaining their applicability in the fabrication of nano-electronic devices.

We have made substantial progress in achieving these objectives by using a relatively little known, simple, convenient and inexpensive "electrospinning" method first reported in a patent in 1934. [2] Since this date a few scattered papers using this technique have appeared in the literature, the number of which has begun to substantially increase during the past ten years. [3-5]

We have previously reported [6] fabrication of the first conducting polymer fibers (diameter ~950 nm to 2,100 nm) of polyaniline doped with d,l camphorsulfonic acid (PAn.HCSA) as a blend in polyethylene oxide (PEO). We were surprised to find that an electronic polymer, such as polyaniline, which might have been expected to be more susceptible to degradation than most conventional organic polymers, survived, without observable chemical or physical change, following the 25,000 V electrospinning fabrication process in air at room temperature.

2. Experimental

The electrospinning technique for the fabrication of submicron to nanometer scale fibers involves a simple, rapid, inexpensive, electrostatic, non-mechanical method in which a polymer solution in a variety of different possible common solvents, including water, is placed in a hypodermic syringe or in a glass pipette, at a fixed distance (5-30 cm) from a metal cathode electrode such as aluminum foil. [3] The positive (anode) terminal of a

---

[*] Corresponding author. Tel. +215-898-8307; fax +215-898-8378;
email: macdiarm@sas.upenn.edu.
[†] For comparison, a human hair is ~ 50,000 nm.

variable high voltage transformer (Gamma High Voltage Research) capable of delivering 30,000 V is attached to the metal tip of the hypodermic syringe or to a copper wire inserted into the polymer solution in the glass pipette, the negative terminal being attached to the aluminum foil target electrode. The tip of the syringe can be placed vertically over the cathode or at any other convenient angle to it. When the voltage applied between the anode and cathode reaches a critical value, e.g. 14,000 V for polyacrylonitrile and a 20 cm separation, the charge overcomes the surface tension of the deformed drop of the suspended polymer solution formed on the tip of the syringe and a jet is produced. Since the polymer molecules all bear the same (positive) charge, they repel each other while traveling in air during a few milliseconds from the anode to cathode and become separated. [5] At the same time, evaporation of the solvent molecules occurs rapidly. Evaporation of solvent is also enhanced because the similarly-charged (positive) solvent molecules repel each other. Under appropriate conditions, *dry, meters-long* fibers accumulate on the surface of the cathode resulting in a non-woven mesh of nano- to micron diameter fibers.

3. Results and Discussion

3.1. Nanofiber Fabrication

Since the submicron fibers (500 -1,600 nm) obtained in our initial work (See Fig. 1) were not classifiable as true "nanofibers," our immediate objective was to break the "nanotechnology barrier" and to consistently and reproducibly fabricate true nanofibers (diameter <100 nm) of an organic polymer.
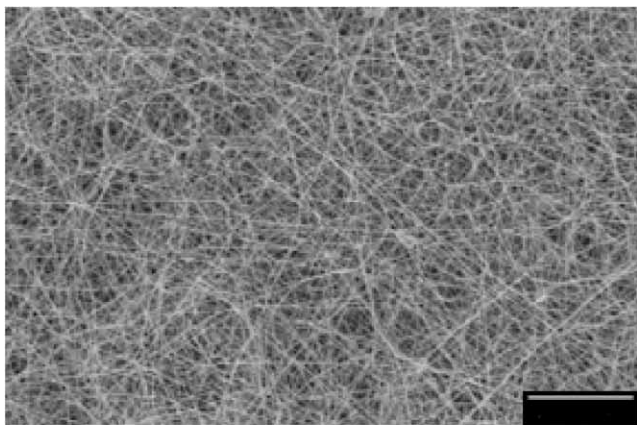

Figure 1. 50 wt% Nanofiber blend of PAn.HCSA fabricated from 2 wt% PAn.HCSA and 2 wt% PEO from chloroform solution at 25,000 V (anode/cathode separation, 25 cm). Scale bar: 100,000 nm. [6]

This was accomplished (see Fig. 2) using a 8 wt% solution of polystyrene (Mw 212,400; Aldrich Co.) in THF (glass pipette orifice: 1.2 mm) at a potential of 20,000 V between the anode and cathode which were separated by 30 cm. The fibers were collected as a mat on an aluminum

target and found by SEM to have diameter characteristics: average, 43.1 nm; maximum, 55.0 nm; minimum, 26.9 nm. Other studies involving polystyrene gave fibers whose diameters were consistently < 100 nm. For example, another sample of polystyrene had the following fiber diameter characteristics: average, 30.5 nm; maximum, 44.8 nm; minimum, 16.0 nm. It might be noted that these data represent a decrease (approximately two orders of magnitude) in fiber diameter as compared to those obtained in our earlier studies (Fig. 1). It might also be noted that the above 16 nm fiber is ~ 30 polystyrene molecules wide. Dimensions of this size will be expected to greatly affect the kinetics, as well as possibly the thermodynamics, of the polymer. It is also of interest to note that a 16 nm fiber such as the one mentioned above lies well within the ~ 4 - 30 nm diameter range of multi-walled carbon nanotubes.[8]
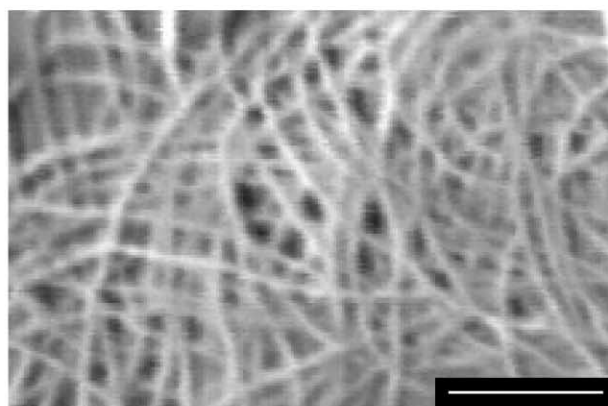

Figure 2. Electrospun fibers of polystyrene (see text). Scale bar: 1000 nm. The extended length of the fibers is clearly visible[7]

3.2. Electronic Polymer Fibers

By using a previously observed method for producing polyaniline fibers [9] we have prepared highly conducting sulfuric acid-doped polyaniline fibers (average, 139 nm; maximum, 275 nm; minimum, 96nm) by placing a ~ 20 wt% solution of polyaniline (Versicon™, Allied Signal) in 98% sulfuric acid in a glass pipette with the tip ~ 3 cm above the surface of a copper cathode immersed in pure water at 5,000 V potential difference. The fibers collect in or on the surface of the water. The conductivity of a single fiber was ~ 0.1 S/cm, as expected since partial fiber de-doping occurred in the water cathode. The diameter and length of the fibers appear (Figure 3) to be sensitive to the nature of the polyaniline used. This is not necessarily surprising since, as is well known, "there are as many different types of polyaniline as there are people who make it!" No great difficulty is foreseen in producing fibers < 100 nm diameter.
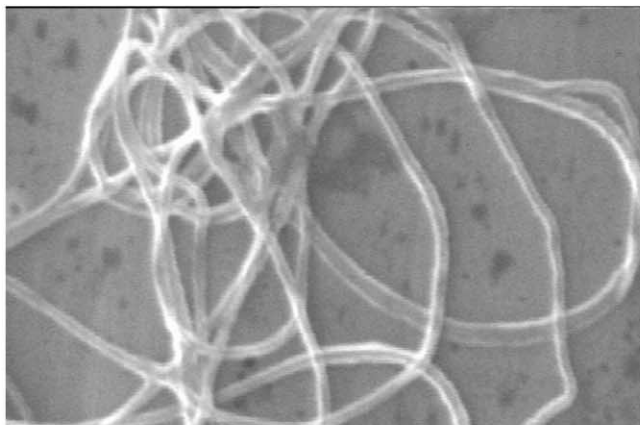
Figure 3. 100% polyaniline fiber with an average diameter of 139 nm.

It is relatively easy to prepare conducting blends of PAn.HCSA in a variety of different conventional polymers such as PEO, polystyrene, polyacrylonitrile, etc. For example, ~ 20 wt% blends of PAn.HCSA in polystyrene (Mw 114,200) are obtained by electrospinning a chloroform solution; fiber diameter characteristics: average, 85.8 nm; maximum, 100.0 nm; minimum 72.0 nm. These fibers are sufficiently electrically conductive that their SEMs may be recorded without the necessity of applying a gold coating.

Separate, individual nanofibers can be collected and examined if so desired. An appropriate substrate—glass slide, silicon wafer or loop of copper wire, etc.—is held between the anode and cathode at a position close to the cathode for a few seconds to collect individual fibers (see Fig. 4).
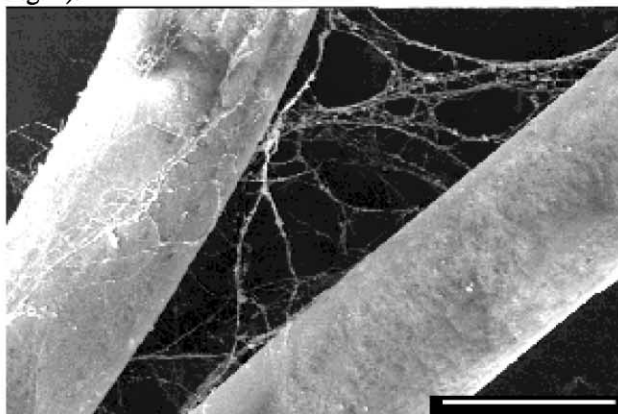

Figure 4. Polystryrene fibers collected on a bent copper wire (magnification 33x) and subsequently coated with a thin layer of polypyrrole by *in situ* deposition from aqueous solution. [13] Scale bar: 1 mm.

The fibers on the copper wires are in a good configuration for certain electrical studies.

Current/voltage (I/V) curves are given in Fig. 5 for a single 419 nm diameter fiber (Fiber 1) of a blend of 50 wt% PAn.HCSA and polyethylene oxide collected on a silicon wafer coated with a thin layer of SiO$_2$. Two gold electrodes separated by 60.3 μm are deposited on the fiber

after its deposition on the substrate. The conductivity (two probe) of Fiber 1 (diameter ~ 600 nm) is ~ 10^{-1} S/cm. The conductivity (two probe) of Fiber 2 (diameter ~ 419 nm) is ~ 10^{-1} S/cm. Non-linear I/V curves may be obtained from some polyaniline samples, possibly caused by the presence
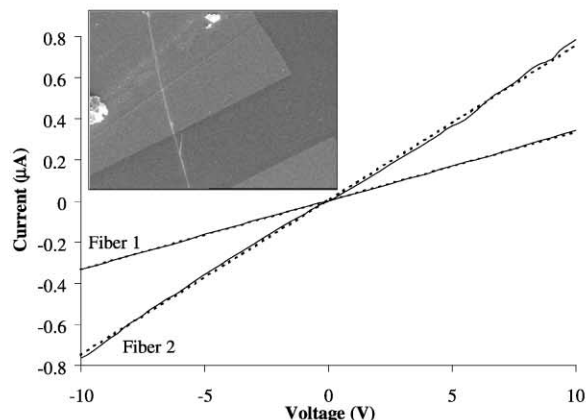

Figure 5. Current/voltage curves of 50 wt% PAn.HCSA/PEO blend nanofiber.

of defect sites induced by imperfections or impurities in the polyaniline. Such imperfections are expected to be more apparent in thin fibers since there are fewer molecular pathways by which charge carriers can by-pass the defect sites.

The (reversible) conductivity/temperature relationship between 295 K and 77 K for a single 1,320 nm fiber containing (72 wt% PAn.HCSA in PEO) spun from chloroform solution is given in Fig. 6. To minimize heating effects the applied voltage was held constant at 10 mV, at
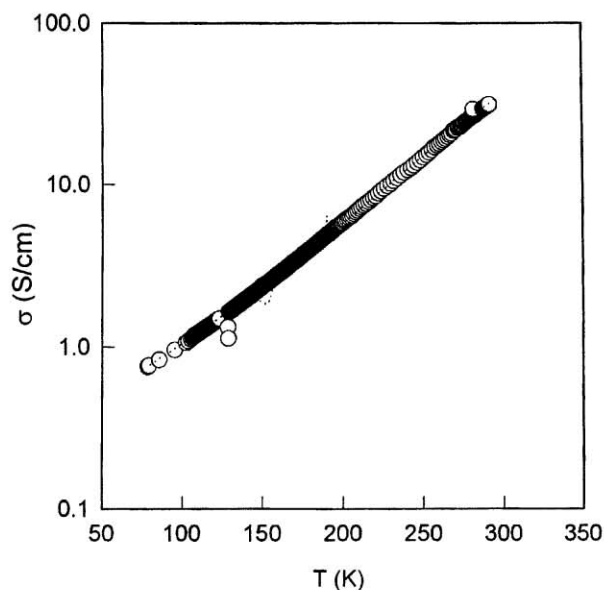

Figure 6. Conductivity/temperature relationship for a 72 wt% blend fiber of PAn.HCSA in PEO (see text).

which value the current is very small. The conductivity (~ 33 S/cm at 295 K) was unexpectedly large for a blend since the conductivity of a spun film of the pure polymer cast

from chloroform solution is only ~ 10^{-1} S/cm. [11] This suggests there may be significant alignment of polymer chains in the fiber [12].

3.3 Nanofibers as Substrates

The large surface to volume ratio offered by nanofibers makes them excellent, potentially useful substrates for the fabrication of coaxial nanofibers consisting of superimposed layers of different materials. Catalysts and electronically active materials can be deposited by chemical, electrochemical, solvent, chemical vapor, or other means, for use in nanoelectronic junctions and devices.

We have found, for example, that polyacrylonitrile nanofibers can be easily and evenly coated with a 20-25 nm layer of conducting polypyrrole (Fig. 7) by immersion in an aqueous solution of polymerizing polypyrrole. [10,13] Analogously, we have found that electroless deposition of metals can also be performed. Polyacrylonitrile fibers, for example, can be evenly coated with gold by treatment with a solution of AuS_2O_3 and ascorbic acid. [14]
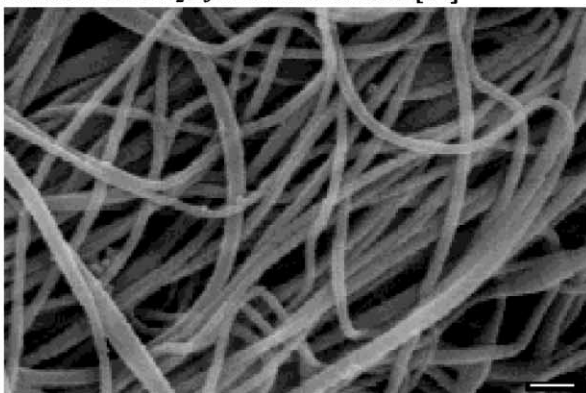

Figure 7. Conducting polypyrrole coated polyacrylonitrile nanofibers. Scale bar: 1000 nm.

3.4 Carbon Nanofibers

As previously reported [15] polyacrylonitrile fibers may be thermally converted to carbon nanofibers with some shrinkage. We have similarly converted a polyacrylonitrile fiber (diameter 750 nm) to a carbon fiber by first heating at 200°C in air for 20 minutes followed by heating at 800°C for 2 hours under nitrogen. A current/voltage curve was obtained for a 600 nm diameter carbon fiber. The controlled conversion of organic electrospun polymer fibers presents interesting opportunities for the fabrication of a variety of carbon nanofibers.

Summary

A new approach to molecular electronics – a general simple, inexpensive, method for controllably generating electronic polymer fibers which are only a few molecules thick is presented as detailed below:

(1) It is possible to consistently fabricate true nanofibers of an organic polymer electrostatically in which the diameters of *all* fibers in a given preparation are < 100nm and hence fall well within the definition of a nanomaterial. Blends of conducting polyaniline in polystyrene which fall within this category have been produced.

(2) Submicron fibers (down to 96 nm) of 100% doped polyaniline were consistently electrostatically generated.

(3) In view of the above findings, it is confidently predicted that true nanofibers of both doped and non-doped electronic polymers can be fabricated such that all fibers in a given preparation have diameters < 100 nm.

(4) The demonstrated fabrication of coaxial cladding of nanofibers with electronic polymers and metals presents the possibility of p/n junctions, Schottky barriers and the like in true nanoelectronic devices.

Acknowledgements

References

[1] "Nanotechnology- A Revolution in the Making – Vision for R&D in the Next Decade," report of the Interagency Working Group on Nanoscience, Engineering, and Technology, March 10, 1999.

[2] A. Formhals, US patent No.1,975,504, 1934.

[3] J. Doshi, D.H. Reneker, J. Electrost. 35 (1999)

[4] P. W. Gibson, H.L. Schreuder-Gibson, D. Riven, AIChE J. 45 (1999) 190.

[5] D.H. Reneker, A. L. Yarin, H.Fong, S. Koombhongse, J. Appl. Phys. 87 (2000) 4531.

[6] I.D. Norris, M.M. Shaker, F.K. Ko and A.G. MacDiarmid, Synthetic Metals, 114(2) (2000) 109.

[7] Measurements of fiber diameter characteristics were completed directly on a high resolution SEM screen and have better accuracy than printed reproductions.

[8] S. Iijima, Nature, 354 (1991) 56.

[9] D.H. Reneker and I. Chun, Nanotechnology, 7(3) (1996) 216.

[10] Z. Huang, P.-C. Wang, A.G. MacDiarmid, Y. Xia, and G. M. Whitesides, Langmuir, 13 (1997) 6480.

[11] Y. Xia, A.G. MacDiarmid, A.J. Epstein, Macromolecules, 27 (1994) 7212.

[12] A.G. MacDiarmid, Y. Min, J.M. Wiesinger, E.J. Oh, E.M. Scherr and A.J. Epstein, Synthetic Metals, 55 (1993) 753; S.J. Pomfret, P.N. Adams, N.P. Comfort, A.P. Monkman, Polymer, 41 (2000) 2265.

[13] R.V. Gregory, W.C. Kimbrell and H.H. Kuhn, Synthetic Metals, 28(1-2) (1989) C823.

[14] A.M. Sullivan and P.A. Kohl, J. Electrochem. Soc.,142(7) (1995) 2250.

[15] I. Chun, D.H. Reneker, H. Fong, X. Fang, J. Deitzel, N.B. Tan K. Kearns J. Advanced Materials, 31 (1999) 36.