Available online at www.sciencedirect.com

SCIENCE DIRECT

Materials Letters 59 (2005) 829–832

materials letters

www.elsevier.com/locate/matlet

Poly(acrylic acid) nanofibers by electrospinning

Bumsu Kim*, Hyun Park, Sung-Hwan Lee, Wolfgang M. Sigmund

Department of Materials Science and Engineering, University of Florida, 225 Rhines Hall, P.O. Box 116400, Gainesville, FL 32611, USA

Received 4 June 2004; received in revised form 14 November 2004; accepted 21 November 2004
Available online 7 December 2004

Abstract

Poly(acrylic acid) (PAA) nanofibers were fabricated by electrospinning into NaCl solution. The effect of the ionic strength of NaCl on the morphology of PAA nanofibers was investigated. The smallest diameter of the PAA nanofiber was prepared with 0.01 M NaCl PAA solutions. At the concentration 1 M NaCl, PAA nanofibers could not be fabricated. The viscosity and conductivity changes were measured with changing the concentration of NaCl. It is suggested that diameter variations may be caused by conductivity and polymer chain conformation changes with varying the concentration of NaCl.

Keywords: Poly(acrylic acid); Nanofiber; Electrospinning; Ionic strength

1. Introduction

It is desirable to reduce the diameter of polymer fibers for obtaining outstanding properties such as large surface areas, flexible functionalities, and mechanical properties. Several potential applications for polymer nanofibers were suggested, such as reinforcement, filtration, cosmetic, clothing, sensor, artificial tissue, and electric devices [1].

Electrospinning is one of the methods to produce nanosize fibers by forming electrically charged jet of polymer solutions from the tips of needles with a high voltage supply [1,2]. The diameter of nanofibers synthesized by electrospinning was controlled by varying some parameters such as solution properties (viscosity, conductivity, and surface tension), ambient conditions (temperature and humidity), hydrostatic pressure in the needle, and electric potential at the tip of the needle [3,4].

Various polymer nanofibers have been synthesized by electrospinning [1]. Recently, materials for electrospun nanofibers have been broadened to ceramic, metal, and composite materials [5–7].

Although many polymer nanofibers were fabricated and some parameters of poly(acrylic acid) (PAA) dissolved water/ethanol solutions for electrospinning have been investigated [8], PAA nanofibers fabrication by electrospinning and the effect of the ionic strength on polyelectrolyte nanofibers have not been reported.

In this study, PAA nanofibers were synthesized by electrospinning. The effect of ionic strength on the morphology of PAA nanofiber was observed. To understand the effect of ionic strength, the variations of conductivity and viscosity with changing the concentration of NaCl were measured.

2. Experimental

All of the following materials were obtained from Aldrich and used as received: poly(acrylic acid) (PAA, M_w ~450,000) and sodium chloride (NaCl, 99%).

Solutions for electrospinning were prepared by dissolving 5 wt.% PAA (pH ~2.5) in deionized water and adding a controlled amount of NaCl (0 M, 0.01 M, 0.1 M, and 1 M).

Electrospinning was performed by applying a high voltage (10 kV) between the needle of syringes containing PAA solutions and a conductive collector. The working distance

* Corresponding author. Tel.: +1 352 846 3343; fax: +1 352 392 6359.
E-mail address: kbs0223@hanmail.net (B. Kim).

0167-577X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2004.11.032

between the tip of needle and the collector was 10 cm. Applied positive voltage to polymer solution was 10 kV. All electrospinning was performed under ambient conditions at 24 °C and 45% RH.

All PAA nanofiber samples were observed by Field Emission Scanning Electron Microscopy (FE-SEM, 6335F, JEOL).

The viscosity and conductivity of PAA solution were measured by using a rheometer (MCR 300 Modular Compact Rheometer, Paar-Physic) and a conductivity meter (AR30, Fisher Scientific). The relative viscosity was calculated as a ratio of the viscosity of prepared PAA solutions to the viscosity of deionized water at the same temperature. All viscosity data were taken at shear rate 20 s^{-1}.

3. Results and discussion

Fig. 1 shows the SEM images of PAA nanofibers fabricated by electrospinning into solutions with different ionic strengths. Magnified PAA nanofibers are shown also. At the concentration of 1 M NaCl, no PAA nanofibers were synthesized. Bead structures were observed from all prepared PAA nanofibers. These bead structures may be caused by the low concentration of PAA in solutions because it was reported that bead structures disappeared by increasing the viscosity of polymer solutions with increasing the concentration of polymers in solutions [4,9]. Tiny branch structures (diameter: 30~40 nm) were observed with 0.1 M NaCl added PAA solutions.

The average diameter and the diameter distribution of PAA nanofibers are determined by FE-SEM picture analysis of 300 PAA nanofibers, as shown in Fig. 2. The smallest average diameter of PAA nanofibers was observed at the concentration of 0.01 M NaCl (79.6 nm). At the concentration of 0.1 M NaCl, the average diameter of PAA nanofibers slightly increased (88.8 nm). Without adding NaCl in PAA solutions, the largest average diameter of PAA nanofibers was observed (104.5 nm).

To understand the effect of the salt on the morphology of PAA nanofibers, the relative viscosity and the conductivity of PAA solutions with different NaCl concentrations were measured as shown in Fig. 3.

With increasing the concentration of NaCl, the relative viscosity slightly decreased. Variations in viscosity may be caused by the chain conformation change of PAA in solution upon adding NaCl. With increasing the ionic strength of the solution, the chain conformation of PAA changes from the extended linear conformation to the coil conformation because PAA is a polyelectrolyte. Although relative viscosity decreases slightly with increasing the amount of NaCl, it is suggested that the range of viscosity change is not a crucial factor to control the diameter change of PAA nanofiber under this experimental condition compared to other's published results [4].

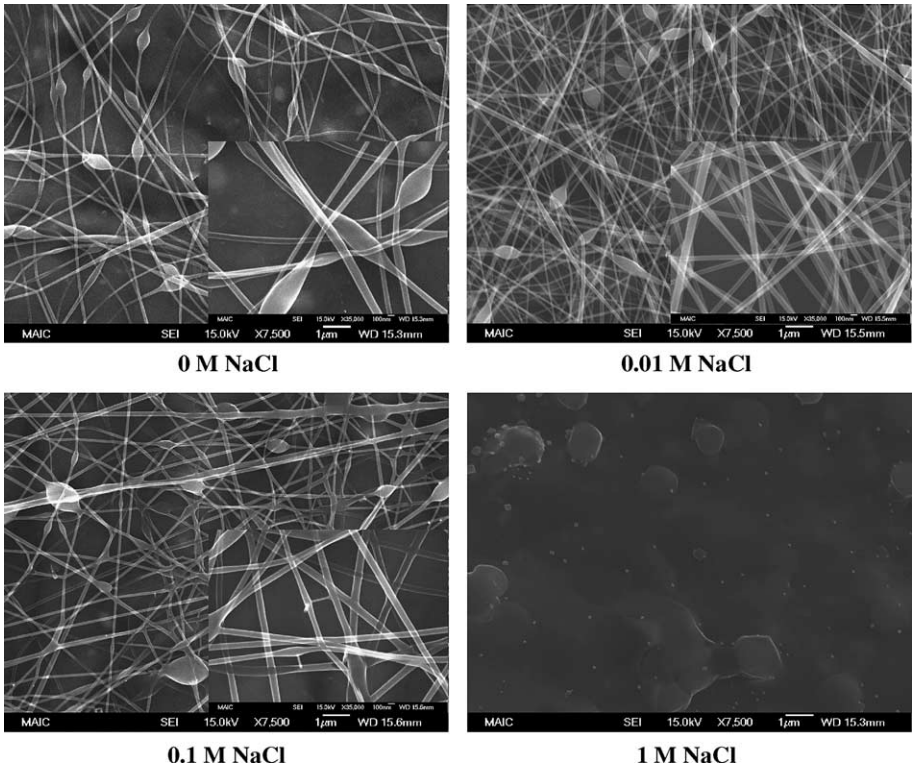

Fig. 1. The SEM images of PAA nanofibers with different concentrations of NaCl.

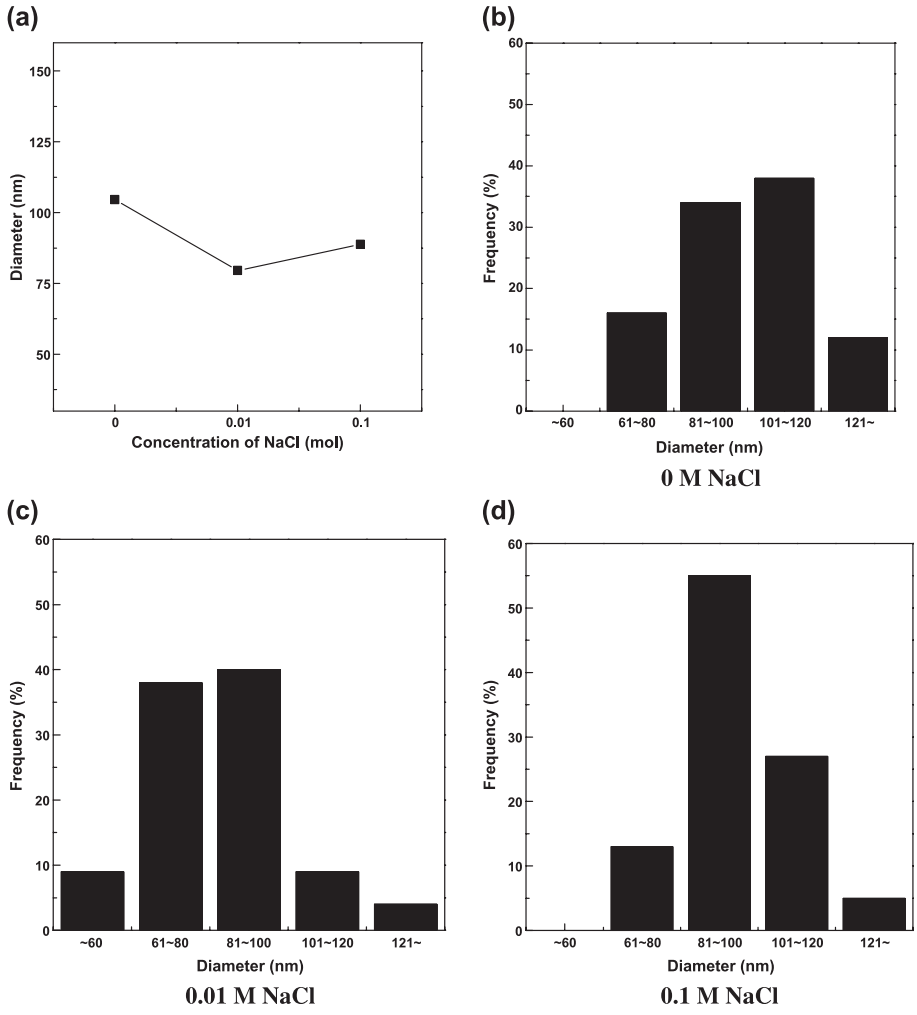

Fig. 2. Average diameter (a) and diameter distribution (b–d) of PAA nanofibers with different concentrations of NaCl.

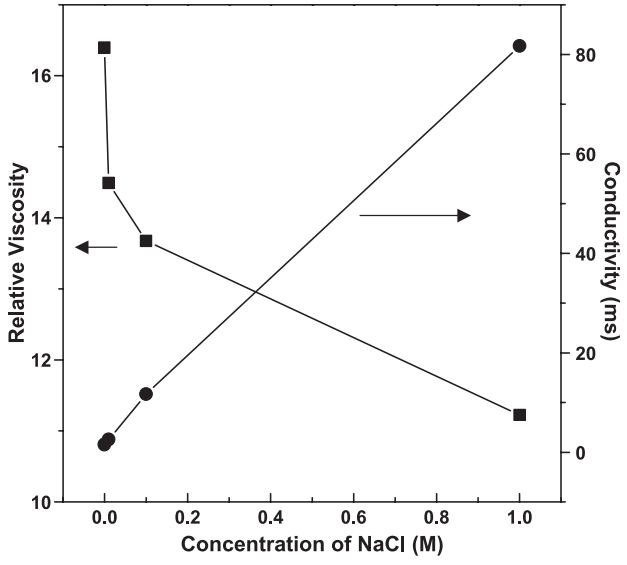

Fig. 3. Relative viscosity (–■–) and conductivity (–●–) changes of PAA solutions with different concentrations of NaCl.

In terms of conductivity, the conductivity increased with increasing the concentration of NaCl. It was reported that the diameter of nanofibers decreased with increasing the conductivity of polymer solutions [10]. However, in the PAA nanofibers, the minimum diameter of nanofibers was observed at the concentration of 0.01 M NaCl with PAA solutions (2.563 ms). With increasing the conductivity by adding 0.1 M NaCl (11.7 ms), the diameter of PAA nanofiber increased. This diameter change may be caused by the chain conformation change of PAA and the rapid increase of the conductivity with increasing the ionic strength. At the concentration of 1 M NaCl, the conductivity may be too high to maintain fiber shapes by balancing surface tension and electric forces (81.71 ms).

4. Conclusions

PAA nanofibers were fabricated by electrospinning with 5 wt.% PAA/water solutions. The effect of ionic strength on the morphology of PAA nanofibers was investigated by measuring the viscosity and the conductivity of PAA

solutions. It is suggested that the characteristic morphology change of PAA nanofiber may be caused by the chain conformation and conductivity changes of PAA solutions with ionic strength changes.

References

[1] Z.M. Huang, Y.Z. Zhang, M. Kotaki, Compos. Sci. Technol. 63 (2003) 2223–2253.
[2] A. Formhals, US Patent 1,975,504, (1934).
[3] J. Doshi, D.H. Reneker, J. Electrost. 35 (1995) 151–160.
[4] Z. Jun, H.Q. Hou, A. Schaper, J.H. Wendorff, A. Greiner, E-Polymers Art. No. 009, 2003.
[5] D. Li, Y.N. Xia, Nano Lett. 3 (2003) 555–560.
[6] D. Li, T. Herricks, Y.N. Xia, Appl. Phys. Lett. 83 (2003) 4586–4588.
[7] Y. Dror, W. Salalha, R.L. Khalfin, Y. Cohen, A.L. Yarin, E. Zussman, Langmuir 19 (2003) 7012–7020.
[8] S.A. Theron, E. Zussman, A.L. Yarin, Polymer 45 (2004) 2017–2030.
[9] H. Fong, D.H. Reneker, J. Polym. Sci., B, Polym. Phys. 37 (1999) 3488–3493.
[10] S.V. Fridrikh, J.H. Yu, M.P. Brenner, G.C. Rutledge, Phys. Rev. Lett. 90 (2003) 144502.