



JOURNAL OF MACROMOLECULAR SCIENCE
Part A—Pure and Applied Chemistry
Vol. A39, No. 10, pp. 1251–1258, 2002

ELECTROSPINNING TECHNOLOGY: A NOVEL APPROACH TO SENSOR APPLICATION

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ABSTRACT

The synthesis, fabrication, fluorescence and fluorescence quenching behavior of fluorescent polymer, polyacrylic acid-poly (pyrene methanol) (PAA-PM) are reported. The Stern-Volmer plots of the electrospun membranes exhibited good linearity for Fe³⁺, Hg²⁺ and DNT and the Stern-Volmer constants K_{sv} are 4.4×10^4 (M⁻¹), 3.5×10^4 (M⁻¹) and 2.9×10^4 (M⁻¹), respectively. These values are one order of magnitude more than those obtained previously from films made by electrostatic layer-by-layer adsorption of the same polymer.

Key Words: Electrospinning; Fluorescence quenching; Optical sensor

INTRODUCTION

Electrospinning has recently gained much attention as a unique technique to fabricate high surface area and highly responsive nanofibrous structures.^[1–6] In electrospinning, a high voltage is applied to create electrically charged jets of a polymer solution, which repeatedly stretch and



split longitudinally into finer jets. These jets dry to form very fine polymer fibers, which are collected on a target as a non-woven membrane. The diameters of electrospun fibers can range anywhere from several micrometers to as narrow as tens of nanometers depending on the polymer and experimental conditions. As a result, electrospun nanofibrous membranes can have a surface area per unit volume of up to two orders of magnitude higher than that of continuous thin films. This high surface area has the potential to provide high sensitivity and fast response times for sensing applications.

Here, we report the preliminary study of electrospun membranes for highly responsive fluorescence quenching-based optical sensor applications. The fluorescent polymer, polyacrylic acid-poly (pyrene methanol) (PAA-PM), was synthesized via covalent attachment of the fluorescent indicator, pyrene methanol (PM), onto polyacrylic acid (PAA). Optical chemical sensors were then fabricated by electrospinning PAA-PM and poly (allylamine hydrochloride) simultaneously in a dual-electrode configuration. The sensing properties of the electrospun membranes to metal ions (ferric and mercuric) and 2,4-dinitro toluene (DNT) were investigated. The synthesis, characterization, electrospinning fabrication and comparison of the sensing properties between the electrospun membranes and electrostatically layer-by-layer (ELBL) assembled films^[7] are presented.

EXPERIMENTAL

Materials

Ferric chloride was obtained from Acros and used as received. All other chemicals were purchased from Aldrich and used without further purification.

Polymer Synthesis (PAA-PM)

A solution of 1,1'-carbonyldiimidazole (CDI, 0.45 g, 2.8 mmole) and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 10 mL of N,N'-dimethylformamide (DMF) was added to a solution of PAA (MW = 50,000 g/mole) (2.0 g, 28 mmole) in 40 mL of DMF. After stirring the solution at 70°C until the evolution of carbon dioxide subsided (30 min), a solution of PM (0.65 g, 2.8 mmole) in 15 mL dimethyl formamide (DMF) was added and the solution was stirred at 70°C for 24 h. The solution was slowly poured with vigorous stirring into ethyl ether to precipitate the polymer. After filtration, the obtained solid was extensively washed with ether and acetone and dried in a vacuum oven for 24 h at 25°C.

Electrospinning

Two spin-dope solutions, that were simultaneously spun, were used for fabrication of the sensors. One consisted of a 26%, by weight, solution of PAA-PM dissolved in DMF. The second spin-dope solution consisted of 12%, by weight, of poly(allylamine hydrochloride) (PAH) in 50%, by weight, of DMF and 38%, by weight, of water. This second spin-dope solution was used as a thermal crosslinker to the PAA-PM to help ensure immobilization and insolubility of the fluorescence indicator in the membranes.

The electrospinning set-up used for these experiments is illustrated in Fig. 1. The two different polymer spin-dope solutions were drawn into two separate glass pipettes and mounted horizontally on an electrically insulated fixture. The distance between the two pipette tips was less than 2 mm. Two live electrode wires from the DC power source (Gamma High Voltage Research, Inc. model HV ES30P/100) were inserted into the pipettes. Two streams of polymer solution intermeshed in the air were collected on a glass slide. The applied electrospinning voltages ranged from 15–20 kv. The distance between the tips and the glass slide was typically 15 to 20 cm. The collection time was about 15 to 30 sec. The electrospun membranes were dried in a vacuum oven at 70°C for 24 h, and then heat-treated for cross-linking at 130°C for 3 h to obtain water insoluble sensing films.

Characterization

UV-visible absorption spectra were recorded using a GBC UV/VIS 916 spectrophotometer. The morphology of the membranes was determined using a scanning electron microscope (Amray 1400). The sensing capabilities of the membranes were determined by measuring the fluorescence quenching

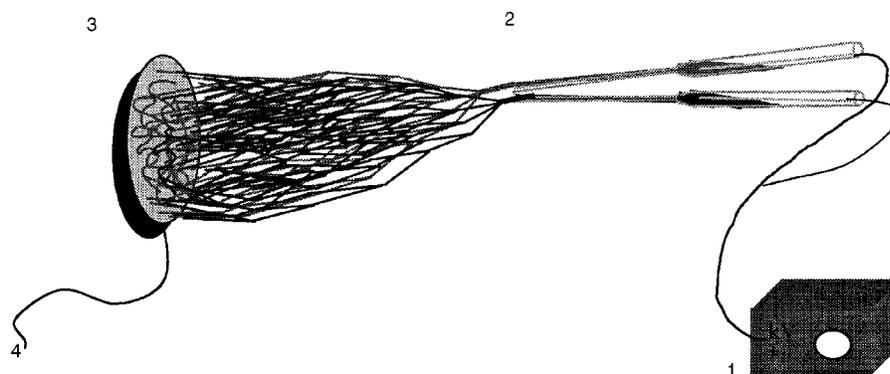


Figure 1. Experimental arrangement for electrospinning (1: power source; 2: polymer spin-dope solutions; 3: collection target; 4: ground).

with a fluorescence spectrofluorometer (SLM-AMINCO Model 8100). The electrospun membrane coated glass slide was fixed in a 1 cm quartz cuvette which was filled with analyte solution. The excitation wavelength was 348 nm. The emission spectra were measured from 400 nm to 600 nm.

RESULTS AND DISCUSSION

Photophysics Property Studies

PAA-PM was synthesized by covalent post functionalization of pyrene methanol (PM) onto poly (acrylic acid) (PAA) as shown in Fig. 2. As expected, the synthesized PAA-PM polymer shows the characteristic UV absorption and emission spectra of the PM indicator as shown in Fig. 3.

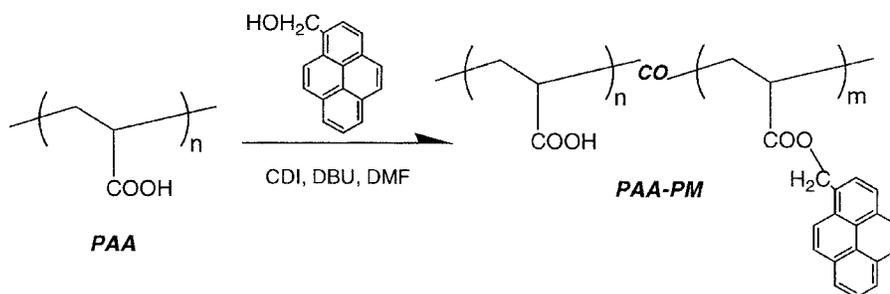


Figure 2. Synthesis scheme for polymer PAA-PM.

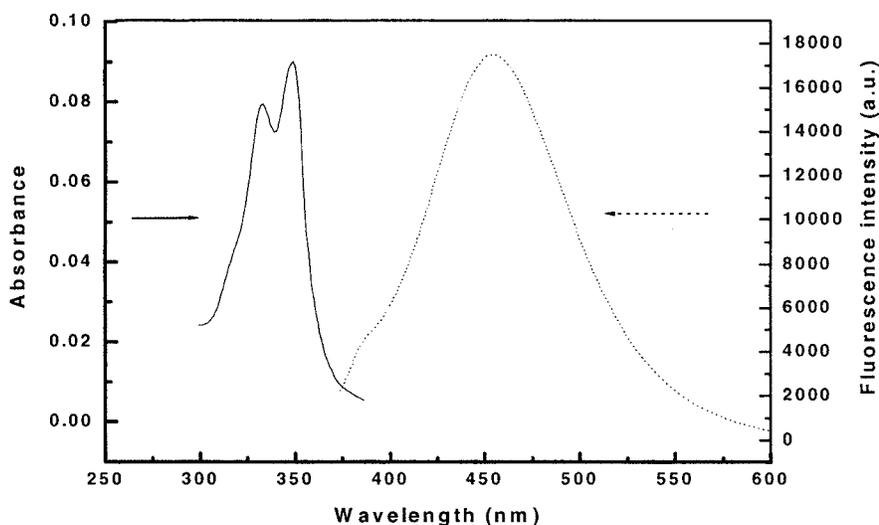


Figure 3. UV absorption and fluorescence emission spectra of PAA-PM.

The amount of functionalization was calculated by comparing integration of the aromatic hydrogen in the indicator with the aliphatic hydrogen in PAA from $^1\text{H-NMR}$ spectroscopy and was determined to be about 7%.

Electrospun Membranes

One of the advantages of electrospinning is its versatility in fabricating nanofibrous membranes with different composition and structure. Different polymers can be electrospun into one membrane either by preparing a spin dope containing all the polymers or spinning different spin dopes separately onto the same target. In this work, three methods were investigated. The first method was preparing one spin dope by mixing PAA-PM with PAH in water and DMF. The obtained solution could not be spun into fiber even if maximum voltage (30 Kv) was applied. It was because the negatively charged PAA-PM reacted with the positively charged PAH in solution, forming a highly viscous jelly structure. The second method was electrospinning the two polymer solutions, PAA-PM and PAH, alternatively to form a multilayer structure. The electrospun membranes obtained could not cross link efficiently and were still water soluble. The third method used is described in the experimental section. The obtained electrospun membranes were robust and water insoluble. An earlier study^[8] has verified that crosslinking between ammonium groups of PAH and carboxylate groups of PAA occurred by formation of an amide bond. The scanning electron microscope (SEM) image of the electrospun membrane of the crosslinked PAA-PM and PAH is shown in Fig. 4. The diameters of the fibers were approximately 100 to 400 nm.

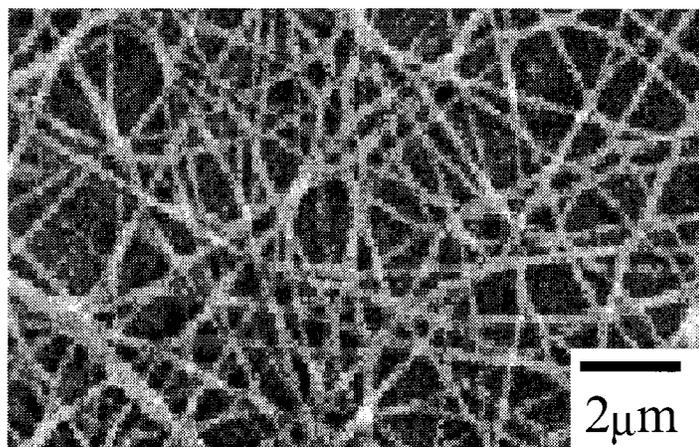


Figure 4. SEM image of electrospun membrane.

Fluorescence Quenching Studies

Electron-deficient metal cations such as Fe^{3+} , Hg^{2+} and nitro aromatic compounds such as DNT and TNT can serve as quenchers for fluorophore. Fluorescence spectra as a function of different concentrations of ferric ion are shown in Fig. 5. It was found that the fluorescence intensities decreased with increasing Fe^{3+} concentration. This fluorescence intensity decrease is expected and believed to be due to the quenching of the PM indicator by the Fe^{3+} ions. Similar behaviors were observed with Hg^{2+} and DNT. The sensing mechanism of this polymer system has been previously studied^[7] and is applied to the electrospun membranes. The quenching follows a conventional “Stern-Volmer” relationship: $I_0/I = 1 + K_{sv}[Q]$, where I_0 and I are the fluorescence intensities in the absence and presence of quencher respectively, $[Q]$ is the quencher concentration, and K_{sv} is the Stern-Volmer quenching constant. The constant K_{sv} defines the efficiency of quenching. When all other variables are held constant, the higher the K_{sv} , the lower the concentration of quencher required to quench the luminescence. The data obtained by performing a Stern-Volmer analysis in each sensor is shown in Fig. 6. Linear plots between concentration of quencher and I_0/I are obtained showing a Stern-Volmer relationship. The Stern-Volmer constant K_{sv} of the electrospun membrane, calculated from the slope of the plot was found to be $4.4 \times 10^4 \text{ (M}^{-1}\text{)}$, $3.5 \times 10^4 \text{ (M}^{-1}\text{)}$ and $2.9 \times 10^4 \text{ (M}^{-1}\text{)}$ for Fe^{3+} , Hg^{2+} and DNT, respectively. This value is one order of magnitude greater than that

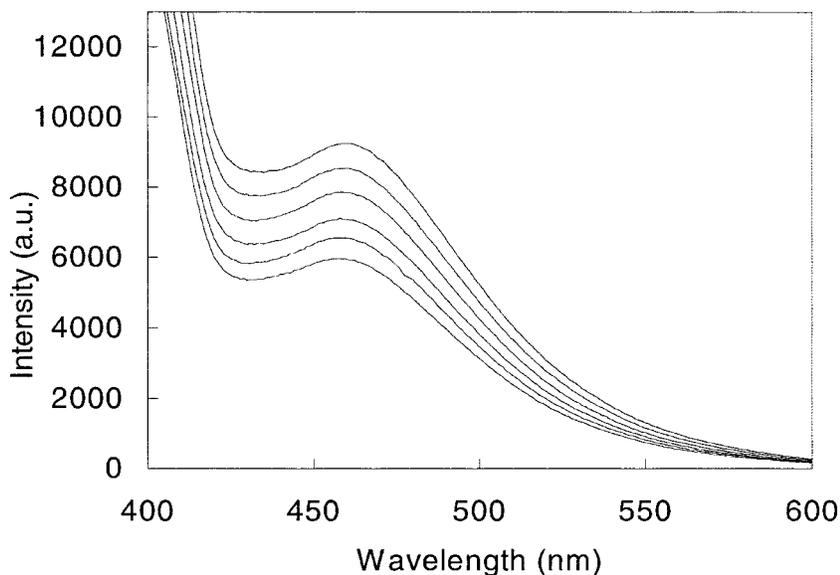


Figure 5. Fluorescence emission spectra of electrospun membranes with varying Fe^{3+} concentration.

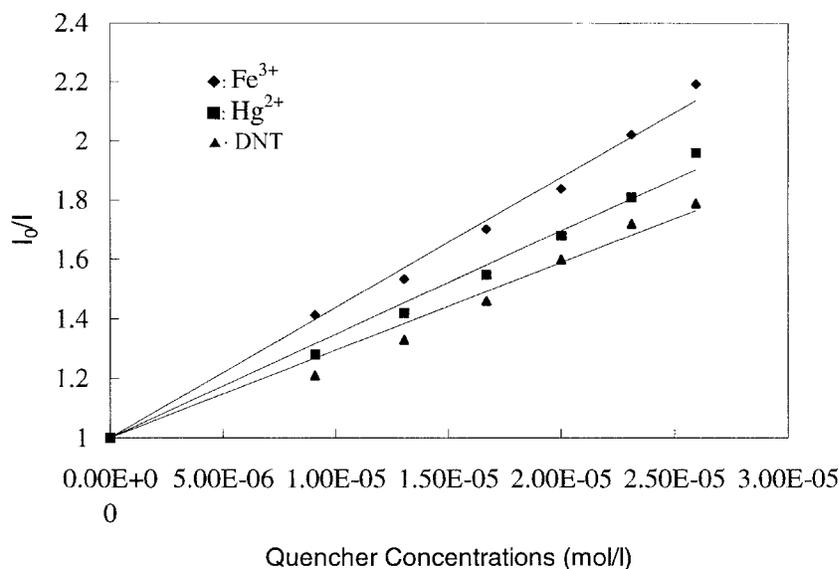


Figure 6. Stern-Volmer plots of electrospun membranes as a function of different quencher concentrations: \blacklozenge : Fe³⁺ \blacksquare : Hg²⁺ \blacktriangle : DNT.

Table 1. Sensitivities of Electrospun and ELBL Self-Assembled Thin Film

	Fe ³⁺	Hg ²⁺	DNT
Electrospun membrane	4.4×10^4	3.5×10^4	2.9×10^4
ELBL film	2.9×10^3	2.6×10^3	8.8×10^2

obtained previously from an ELBL self-assembled thin film sensor.^[7] Table 1 is the summary of the comparison. This significant enhancement of the sensitivity of the sensor is attributed to the higher surface area of the electrospun membrane.

CONCLUSION

The preliminary results show that electrospinning is a very promising, facile, and effective technique for fabricating sensor devices. Compared to continuous thin films, electrospun nanofibrous membranes can offer enhanced reactivity and sensitivity and exciting new opportunities in optical sensing.

ACKNOWLEDGMENTS

Financial support from the U.S. Army is acknowledged. The authors are grateful to Dr. J. He, Dr. S. Balasubramanian, and Dr. L. Li for discussions of optical sensing. The authors also recognize Professor C. Sung and Ms. B. Kang for the SEM images and Dr. H. Schreuder-Gibson for advice and assistance with electrospinning. This work is dedicated to Professor S. K. Tripathy.

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