

Pyrene-Doped Electrospun PMMA-PVC Fibers for Ferric Ion Detection

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ABSTRACT: Electrospun fibers for ferric ion (Fe^{3+}) detection were prepared from solutions of poly(methyl methacrylate) (PMMA), poly(vinyl chloride-co-vinyl acetate-co-vinyl alcohol) ((90 : 4 : 6), PVC terpolymer), and pyrene. The effects of PVC terpolymer content (0, 10, 20, 30, and 40% by weight of PMMA) and electrospinning conditions on fiber size and morphology were studied using scanning electron microscopy. Uniform fibers were obtained from all compositions, and fiber sizes slightly increased with PVC terpolymer content. At 40% PVC, fiber breakage and pyrene clusters were observed. The suitable pyrene content in electrospun fibers was found to be 20%. The ratio of fluorescence intensities of fibers with 30% PVC and 20% pyrene before and after (F_0/F) immersion in 1.0 mM Fe^{3+} solution was 1.36. The effect of Fe^{3+} concentrations (0–5.0 mM) on quenching ability was investigated. An excellent Stern–Volmer quenching relationship was found with K_{SV} of $2.26 \times 10^2 \text{ M}$. Fibrous sensor exhibited a highly sensitive response toward Fe^{3+} over Cu^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , and Ag^+ . © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3205–3211, 2013

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INTRODUCTION

Monitoring trace metal ions is of great interest in biomedical and environmental fields. Iron is a key element in metabolic processes including oxygen uptake, oxygen and drug metabolism, adenosine-triphosphate production, DNA synthesis, and electron transfer of almost all living organisms.^{1,2} High levels of Fe^{3+} may induce various biological disorders and become toxic for organisms. Therefore, it is important to develop probes to monitor iron traces in food and water samples. In addition, analysis traces of iron would help understanding the biochemical cycling in the ocean or atmosphere.³

Among metal ion determination methods, fluorescence method has drawn a lot of interest. In this method, absorption and/or emission responses of fluorophores resulting from interaction with metal ions are analyzed. The detection is mainly based on three observable changes in fluorescence emission by fluorophore, which are fluorescence enhancement, fluorescence quenching, and a shift in the emission maximum. The first approach relies on the use of a fluorophore that has no or little fluorescence in the absence of the target metal ion, which becomes fluorescent upon an introduction of the metal ion.^{4,5} The second approach is the opposite. The last approach involves a shift in the emission

maximum of the spectrum depending on the presence of the target metal ion.⁶ Metal ion sensors using the quenching of fluorescence by metal ions have been reported by several groups.^{3,7,8}

Recent studies reveal that nanoscale sensing membranes provide a higher sensitivity over thin films with the same composition. A higher sensitivity of nanoscale sensing membranes over thin films is most likely due to the high-surface area-to-volume ratio. The surface area of electrospun fibrous membranes can be one to two orders of magnitude greater than that of continuous thin films.⁹

Electrospinning is a simple method to produce fibrous materials with diameters ranging from nanometers to micrometers.¹⁰ An electrospinning process starts by applying a high voltage to a polymer solution, and a conical drop called the Taylor cone is formed at the tip of a needle. Once electrostatic forces overcome the surface tension of the solution, a polymer jet is produced. The jet is elongated and later deposited on a grounded collector. The spinnability depends on several parameters such as solution viscosity, surface tension, conductivity, and processing conditions.

Electrospun fibers have found applications in sensing devices due to the ease of preparation and the highly sensitive

detection.^{11–14} Electrospun fibers of poly(methyl methacrylate) (PMMA) and ethyl cellulose with *N*-3-(4-(dimethylamino phenyl)allylidene)isonicotinohydrazide as an embedded fluorophore showed 6–10-folds higher in sensitivity to Cu^{2+} than those of the continuous thin films.¹⁵ Wang et al.¹⁶ reported a highly responsive optical fiber sensor for Fe^{3+} , Hg^{2+} , and 2,4-dinitrotoluene based on immobilizing pyrene methanol to poly(acrylic acid). Pyrene was chosen as a fluorescent indicator due to its large Stokes shift, high-quantum yield, strong absorbance, excellent photostability and lifetime, and relatively nontoxicity.

In this work, electrospun fibers prepared from solutions of PMMA, poly(vinyl chloride-*co*-vinyl acetate-*co*-vinyl alcohol) (PVC terpolymer) and pyrene were investigated as an optical sensor for Fe^{3+} . PMMA was chosen due to its flexibility, easy electrospinnability, and low cost. The introduction of PVC would enhance mechanical properties along with thermal and chemical resistivities with good compatibility with PMMA. The effects of PVC terpolymer content and electrospinning conditions on fiber size and morphology were studied using scanning electron microscopy. The sensitivity and selectivity toward Fe^{3+} and other metal ions were investigated.

EXPERIMENTAL

Materials

PMMA (average MW 120,000), poly(vinyl chloride-*co*-vinyl acetate-*co*-vinyl alcohol) (PVC : PVAc : PVA = 90 : 4 : 6, average M_n 20,000), and pyrene (98%) were purchased from Sigma-Aldrich (USA). Iron (III) nitrate nonahydrate and cobalt (II) nitrate were purchased from Merck (USA). Magnesium nitrate hexahydrate and *N,N*-dimethylformamide (DMF) were purchased from Fluka Chemical (USA). Zinc chloride, copper (II) nitrate, nickel (II) sulfate hexahydrate, and silver nitrate were purchased from Carlo Erba Reagents (Thailand), Ajax Finechem (Thailand), Guangdong Guanghua Chemical Factory Co. (China), and Poch S.A. (Poland), respectively. All chemicals were used as received.

Characterization

UV-vis spectrum of pyrene in tetrahydrofuran was measured on a spectrophotometer (Agilent 8453) in the range of 200–400 nm. Emission spectra were recorded using an RF-5301PC spectrofluorometer (Shimadzu) with excitation and emission slit widths of 3 nm (low sensitivity). Fiber morphology was studied using a scanning electron microscope (LEO 1450VP, UK). The average diameters of the fibers were determined by analyzing 200 fibers in each micrograph using WCIF ImageJ program.

Fiber Preparation

An electrospun solution was prepared by dissolving 30 wt % PMMA in DMF. Desired amounts of PVC terpolymer (10, 20, 30, or 40% by weight of PMMA) and pyrene (1, 5, 10, or 20% by weight of PMMA and PVC) were added. The solution was stirred overnight to ensure adequate mixing before loading into a plastic syringe equipped with a 23-gauge stainless steel needle, connected to a high-voltage supply [DEL high-voltage (0–100 kV), DEL Electronics Corp.]. The polymer solutions were spun at a flow rate of 3.0 mL/h using a syringe pump (TERUMO Terufusion Syringe pump TE-331, Japan). A piece of flat

aluminum foil was placed 10, 15, or 20 cm below the tip of the needle. The positive voltage applied was 13.0, 15.0, or 18.0 kV. All experiments were performed at room temperature.

Sensitivity Study

Similar to previous reports,^{15,17} response performance of the fibers toward Fe^{3+} ions was carried out as follows. The nanofibers deposited on aluminum substrate were cut into 1 cm × 1 cm pieces, and fluorescence emission was measured. The excitation wavelength was 336 nm, and emission data were collected in the wavelength region of 350–650 nm. The maximum emission at 465 nm was recorded (F_0). The fibers were then immersed into aqueous ferric nitrate solutions with concentrations ranging from 1.0 to 5.0 mM for 30 min. After thorough washing with water, the fibers were dried before fluorescence emission measurements (F). The mean of three measurements was used for each sample, and the reported F_0/F value was the mean of two replicates.

Selectivity and Interference Studies

To investigate the selectivity of the fibers toward metal ions, 1.0 mM aqueous solutions of metal ions, including Cu^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , and Ag^+ , were prepared. Sensing performance was carried out as described for Fe^{3+} . Aqueous solutions containing both Fe^{3+} (1.0 mM) and other metal ion (1.0 mM) were used in a study of interference effect.

RESULTS AND DISCUSSION

Electrospinning and Fiber Morphology

The intrinsic viscosity, $[\eta]$, can be related to the molecular weight (M) of a linear polymer by Mark-Houwink-Sakurada equation:¹⁸

$$[\eta] = KM^a$$

where K and a are Mark-Houwink parameters. The critical chain overlap concentration, c^* , of 120 k PMMA solution in DMF at 25°C was calculated by the criteria $c^* \sim 1/[\eta]$ and found to be 2.8 wt % using K and a values reported in the literature ($K = 0.015 \text{ cm}^3/\text{g}$ and $a = 0.667$). Previous study by Gupta et al.¹⁹ showed that uniform fibers were observed at $c/c^* \sim 10$ for broad molecular weight distribution PMMAs. In this study, electrospinning of 30 wt % PMMA solutions with $c/c^* \sim 10.7$ at 15.0 kV with working distance of 15.0 cm also provided uniform fibers. SEM images of PMMA/pyrene (20%)/PVC fibers containing different amounts of PVC ranging from 0 to 40% were shown in Figure 1, and fiber diameter distributions were shown in Figure 2. Bead-free fibers were obtained from all compositions. The average diameter of fibers containing only PMMA and 20% pyrene was 2.0 μm . Fiber size slightly increased with increasing PVC terpolymer contents. This observation could be attributed to the increase in polymer concentration, leading to the increase in solution viscosity. The high viscosity results in a larger polymer jet and a consequent deposition of fibers with a larger diameter.²⁰ At low-PVC terpolymer contents, that is, 0, 10, and 20%, fiber mats were light and difficult to handle. At 40% PVC, fiber breakage was observed in SEM image due to brittle and rigid nature of PVC. In addition, pyrene clusters were shown, indicating inhomogeneous mixing. Therefore, 30% PVC was chosen for further investigations. To

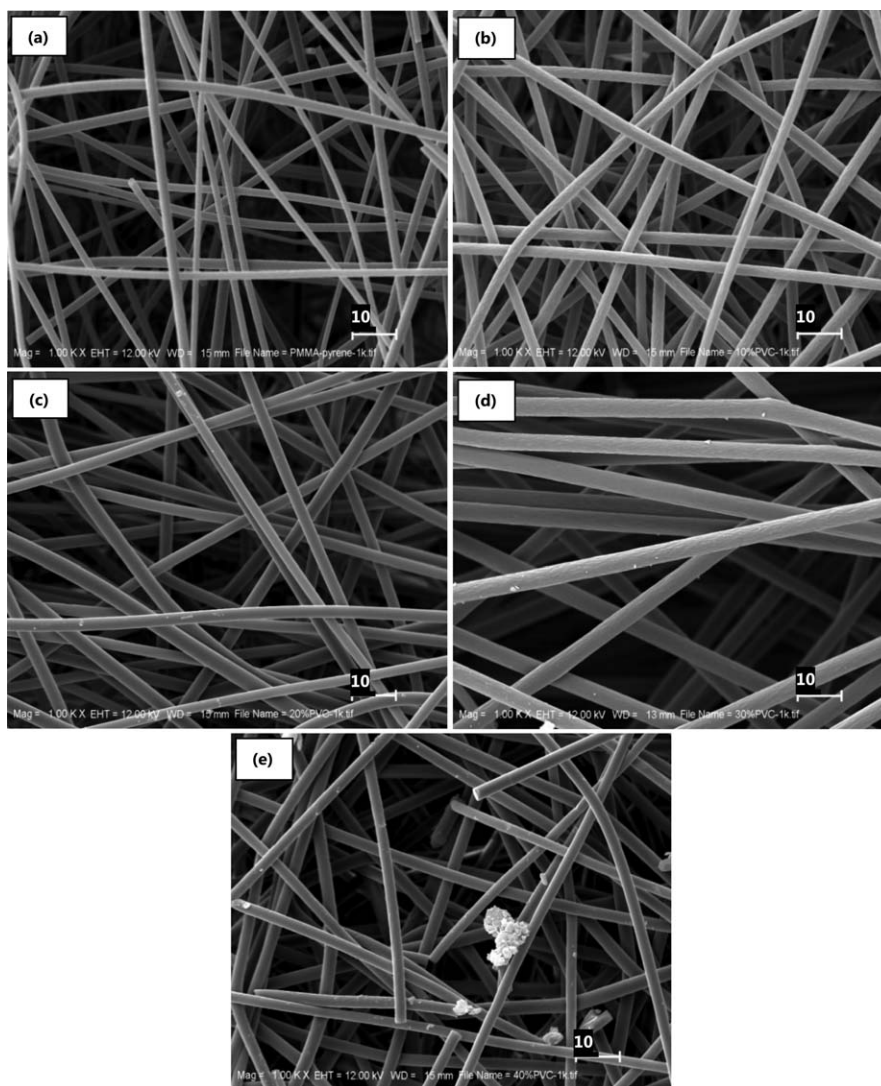


Figure 1. SEM images (1 k magnification) of electrospun fibers with various PVC terpolymer contents. (a) 0, (b) 10, (c) 20, (d) 30, and (e) 40%.

obtain optimal electrospinning conditions, voltage and working distance were varied from 13.0 to 18.0 kV and 10 to 20 cm, respectively. SEM images of fibers obtained with these conditions were shown in Figure 3. Results showed that a voltage of 15.0 kV with working distance of 15.0 cm and a voltage of 15.0 kV with working distance of 20.0 cm were the suitable electrospinning conditions for producing smooth and uniform fibers. Therefore, fibers with 30% PVC terpolymer prepared at 15.0 kV with working distance of 15.0 cm were chosen for metal ion sensing study. The average thickness of the fiber mat was 0.30 ± 0.05 mm.

Sensing Performance

UV-vis absorption spectrum of pyrene solution in Figure 4 illustrated strong sharp bands at 308, 319, and 336 nm, corresponding to three vibrational subbands of single electron transfer ($S_0 \rightarrow S_2$).^{21,22} Emission spectra of pyrene solution and pyrene-doped fibers with 30% PVC terpolymer were also shown

in Figure 4. The maximum emission at 465 nm could be related to pyrene excimers, that is, pyrene dimers or higher aggregates.^{23,24} The emission spectrum of fibers showed no shift in maximum emission compared to that of pyrene solution, suggesting no further formation of pyrene aggregation through π - π stacking interaction.

The effect of pyrene content in electrospun fibers on fluorescence emission was studied by varying the amounts of pyrene from 1 to 20% by weight of PMMA and PVC. The emission spectra in Figure 5 showed two major bands. The first band comprised multiple emission peaks between 370 and 420 nm, which could be ascribed to the emission from singlet excited pyrene (monomer).²⁵ The second band at 465 nm could be ascribed to the emission from excited pyrene excimers as described earlier. At low levels of pyrene, the band corresponding to pyrene monomer was dominant, and at high levels of pyrene, excimer band was dominant. Pyrene content of 20%

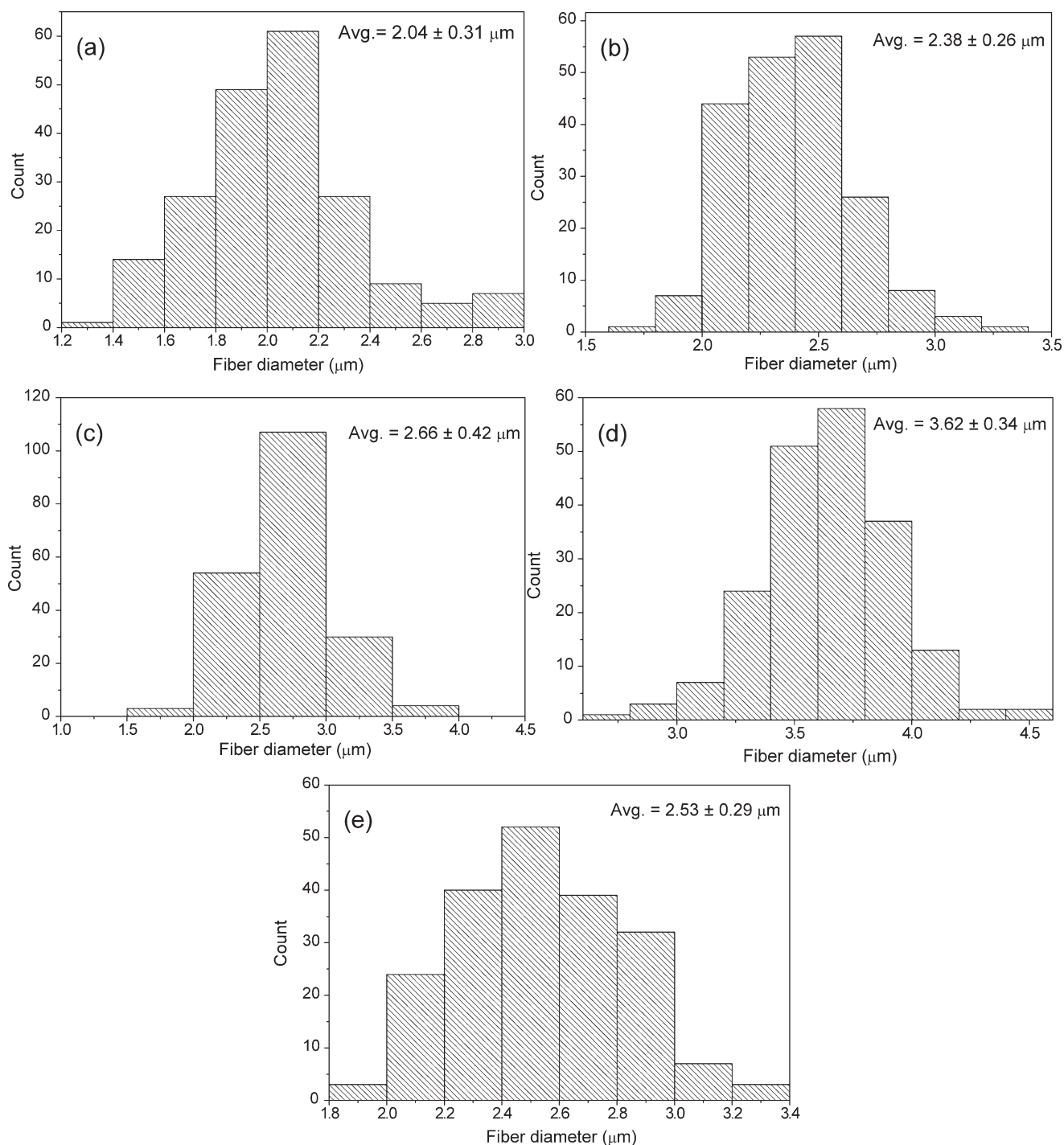


Figure 2. Size distributions of fibers with (a) 0, (b) 10, (c) 20, (d) 30, and (e) 40% PVC terpolymer.

was selected for further studies due to the high-fluorescence intensity of the excimer peak.

Fluorescence quenching can be described by Stern–Volmer equation

$$F_0/F = 1 + K_{sv}[Q]$$

where F_0 and F are fluorescence intensities in the absence and in the presence of quencher, respectively. K_{sv} is Stern–Volmer

constant, and $[Q]$ is the concentration of quencher. The ratio of fluorescence intensities at 465 nm of fibers with 30% PVC terpolymer and 20% pyrene before and after immersion in 1.0 mM Fe^{3+} solution (F_0/F) was 1.36. The quenching of fluorescence is most likely due to interactions of electron-rich dye, pyrene, and electron-deficient quencher, Fe^{3+} , via a photoinduced electron transfer mechanism and/or electronic energy transfer.²⁶ Figure 6(a) showed a change of fluorescence

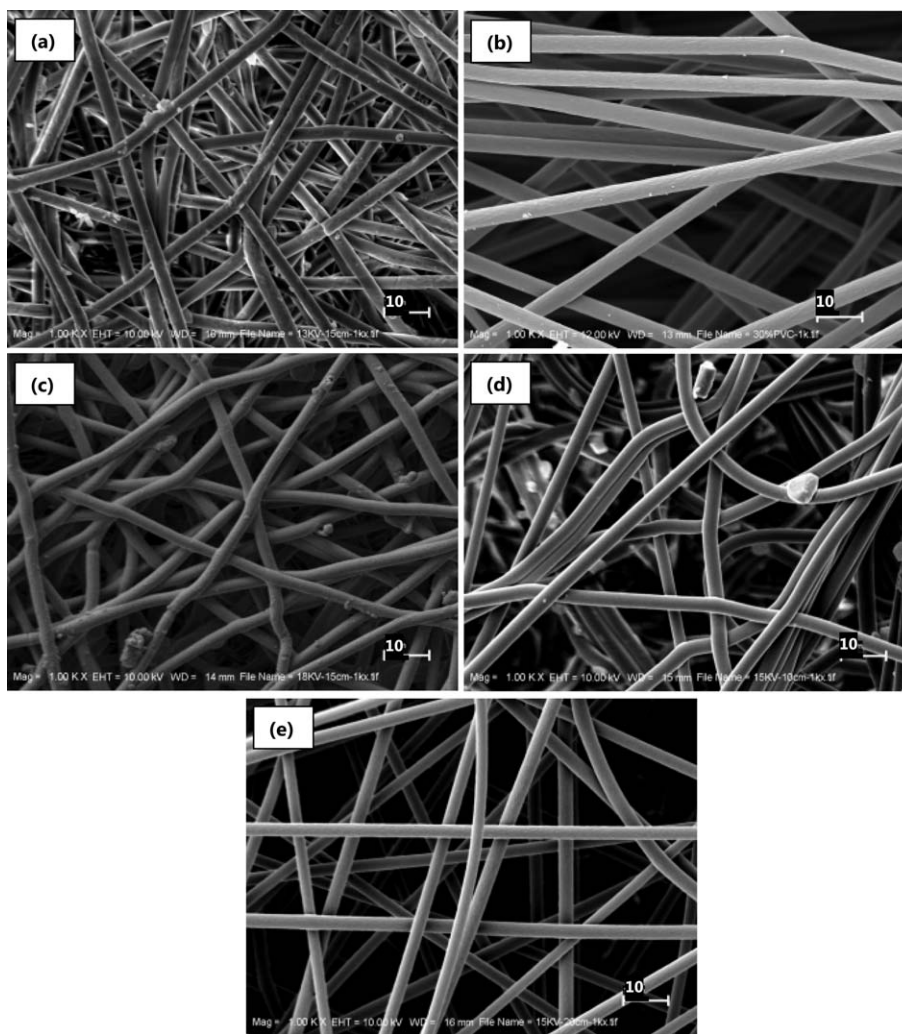


Figure 3. SEM images (1 k magnification) of fibers obtained with various electrospinning conditions. (a) 13.0 kV, 15 cm, (b) 15.0 kV, 15 cm, (c) 18.0 kV, 15 cm, (d) 15.0 kV, 10 cm, and (e) 15.0 kV, 20 cm.

intensity of the fibers as a function of Fe^{3+} concentration. It was found that the intensity decreased with the introduction of Fe^{3+} and gradually decreased with increasing Fe^{3+} concentration. Linear plot between Fe^{3+} concentration and F_0/F is shown in Figure 6(b). K_{sv} calculated from the slope of the plot was $2.26 \times 10^2 M$.

Selectivity and Interference Studies

The selectivity of the sensing fibers was evaluated by immersing the fibers into 1.0 mM aqueous solutions of Cu^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , and Ag^+ for 30 min. After thorough washing with water, fluorescence emission was measured. Figure 7 showed that the fibers were capable of determining Fe^{3+} ions with a high selectivity over other metal ions. F_0/F values for Fe^{3+} , Cu^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , and Ag^+ were 1.36, 1.05, 1.04, 1.00, 1.10, 1.07, and 1.10, respectively. The interference effect of other metal ions on quenching ability of Fe^{3+} was also studied. Figure 8 showed that the coexistence of selected ions did not significantly interfere with Fe^{3+} binding to the chromophore.

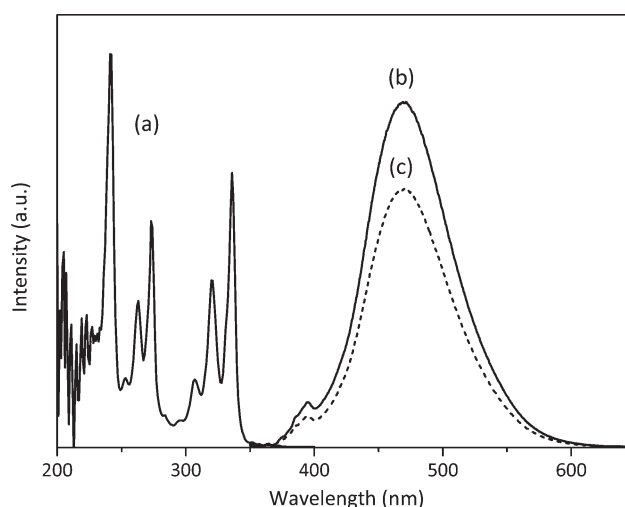


Figure 4. Absorption spectrum of pyrene in THF (a), emission spectrum of pyrene in chloroform (b), and emission spectrum of PMMA/pyrene/PVC fibers (c) ($\lambda_{\text{Ex}} = 336 \text{ nm}$).

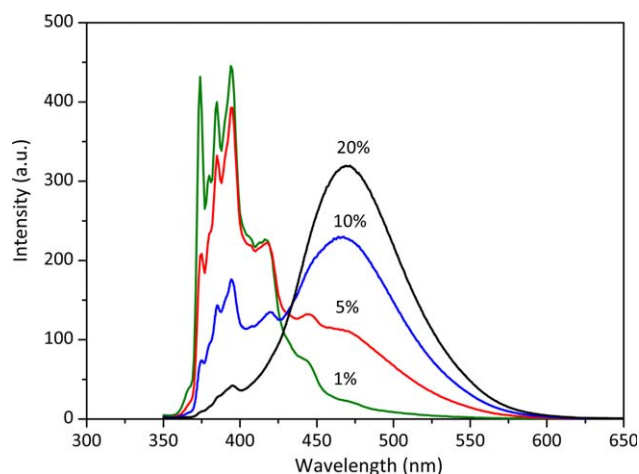


Figure 5. Emission spectra of PMMA/30% PVC fibers with various pyrene contents ($\lambda_{\text{Ex}} = 336$ nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

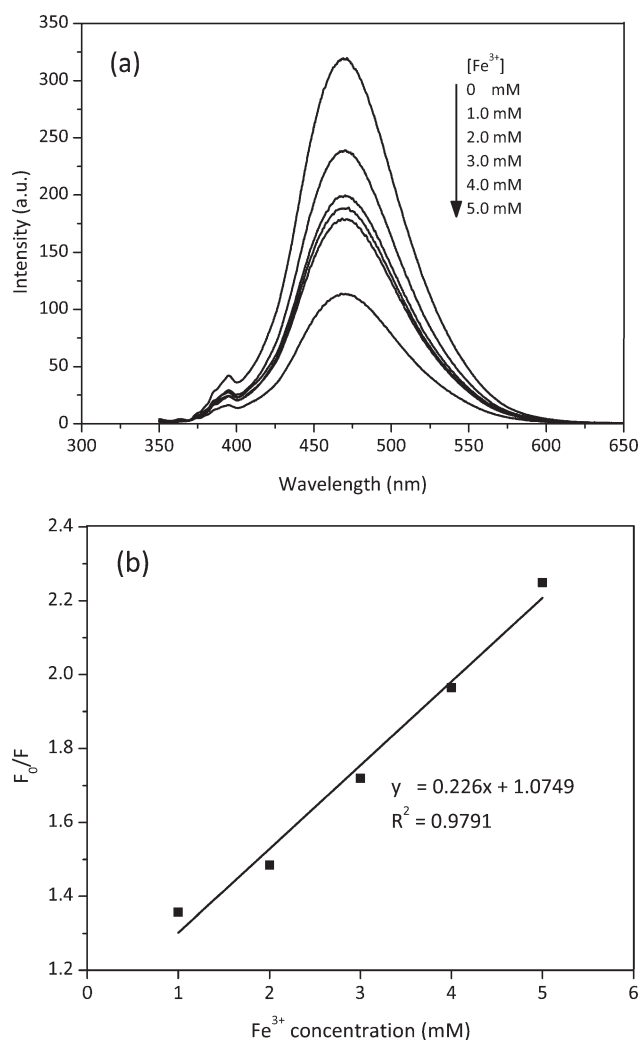


Figure 6. (a) Fluorescence spectra change of fibers with 30% PVC terpolymer and 20% pyrene as a function of Fe^{3+} concentration; $[\text{Fe}^{3+}] = 0\text{--}5.0$ mM (from top to bottom). (b) Stern-Volmer plot of the electrospun fibers in response to Fe^{3+} . ($\lambda_{\text{Ex}}/\lambda_{\text{Em}} = 336/465$ nm).

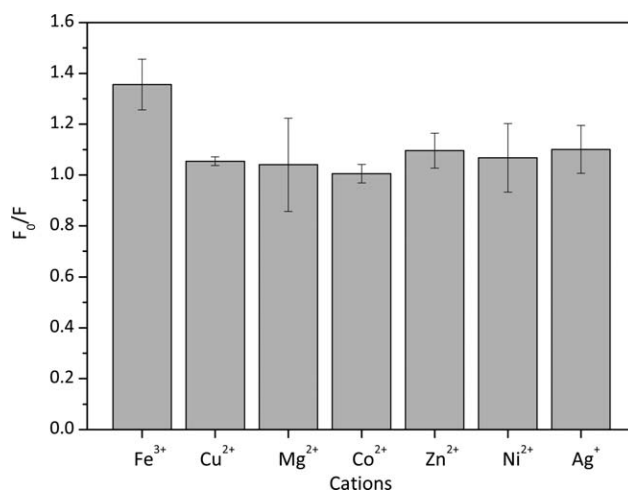


Figure 7. Responses of electrospun fibers to 1.0 mM solutions of various metal cations. ($\lambda_{\text{Ex}}/\lambda_{\text{Em}} = 336/465$ nm).

CONCLUSIONS

This work provided a simple and low-cost approach to fabricate electrospun fibers for Fe^{3+} detection from solutions of PMMA, PVC terpolymer, and pyrene. PVC contents were varied from 0 to 40%, and it was found that all compositions provided uniform fibers. Fiber sizes slightly increased with PVC loadings. Fibers containing 30% PVC and 20% pyrene prepared at 15.0 kV with working distance of 15.0 cm were found to be suitable for sensing study. The ratio of fluorescence intensities of the fibers before and after immersion in 1.0 mM Fe^{3+} solution (F_0/F) was 1.36. Upon increasing Fe^{3+} concentration, emission intensity decreased gradually. Based on Stern–Volmer equation, K_{SV} was calculated to be $2.26 \times 10^2 M$. The prepared fibers exhibited a highly sensitive response toward Fe^{3+} over Cu^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , and Ag^+ . The coexistence of these metal ions did not significantly affect the quenching ability of Fe^{3+} .

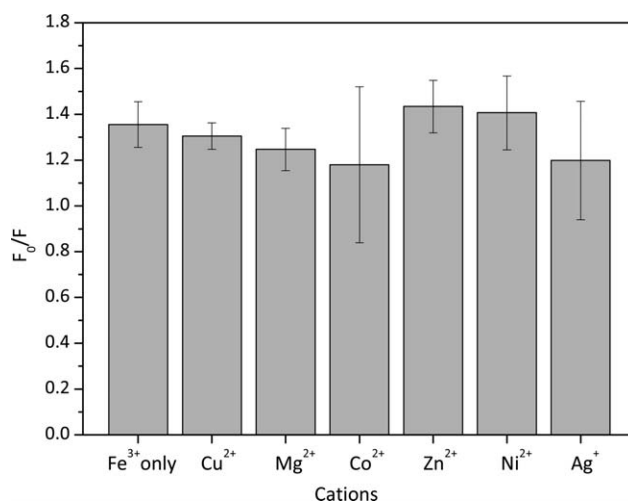


Figure 8. Quenching efficiency of fibers after being immersed into aqueous solution of Fe^{3+} (1.0 mM) only, and aqueous solution containing both Fe^{3+} (1.0 mM) and Cu^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , and Ag^+ (1.0 mM) ($\lambda_{\text{Ex}}/\lambda_{\text{Em}} = 336/465$ nm).

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