Final Report

Project Title : Electrospun fibers from pyrene-functionalized copolymers for ferric ion detection

By Asst.Prof.Surangkhana Martwiset

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This project granted by the Thailand Research Fund

Abstract

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Project Period : 3 June 2013 – 2 June 2015

Abstract:

Monitoring iron traces in food and water samples is of great interest as high levels of ferric ion may induce various biological disorders and become toxic for organisms. Fluorescence technique was chosen as analytical tool due to its simplicity and sensitivity. Fluorescence quenching-based sensing membranes for Fe^{3+} detection were prepared using pyrene as a fluorescent indicator embedded in a polymer matrix. 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. Two sensing materials were prepared. The first materials were electrospun fibers from poly(methyl methacrylate) (PMMA), poly(vinyl chloride-*co*-vinyl acetate-*co*-vinyl alcohol) and pyrene. The fibers showed good sensitivity toward Fe^{3+} with the ratio of fluorescence intensities before and after immersion in 1.0 mM Fe^{3+} solution (F_0/F) of 1.36. The second materials were solvent-cast membranes from polyvinyl chloride (PVC) and PVC-*graft*-polystyrene (PS). The membrane prepared from PVC-*g*-PS showed higher sensing abilities than that from PVC with the F_0/F value of 1.39. This could be due to pi-pi stacking between the phenyl side chains of PS and pyrene, which facilitated the interaction between pyrene and Fe^{3+}. In addition, introduction of porous structures to PVC membrane also enhanced the sensing performance. All prepared materials exhibited highly sensitive and selective responses toward Fe^{3+} over other selected metal ions. Moreover, a good reversibility of quenching and regeneration was obtained.

Keywords : Electrospinning, Fibers, Grafting, Polyvinyl chloride, Porous materials

The final report will be divided into two small projects:

1. Pyrene-doped electrospun PMMA-PVC fibers for ferric ion detection

2. Enhancing performance of optical sensor through the introduction of polystyrene and porous structures

1. Pyrene-doped electrospun PMMA-PVC fibers for ferric ion detection

1. 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 (SEM). 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 x 10^2 M^{-1}. Fibrous sensor exhibited a highly sensitive response toward Fe^{3+} over Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Ag^{+}.

2. Executive summary

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.

3. Objective

To prepare electrospun fibers as sensing materials for Fe^{3+}

4. Research methodology

Materials

Poly(methyl methacrylate) (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 (U.S.A.). Iron (III) nitrate nonahydrate and cobalt (II) nitrate were purchased from Merck (U.S.A). Magnesium nitrate hexahydrate and *N, N*-dimethylformamide (DMF) were purchased from Fluka Chemical (U.S.A.). 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. Ltd (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 a 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 prior to 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

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 x 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 mM to 5.0 mM for 30 minutes. After thorough washing with water, the fibers were dried prior to 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 mM) and other metal ion (1.0 mM) were used in a study of interference effect.

5. Results and discussions

Electrospinning and fiber morphology

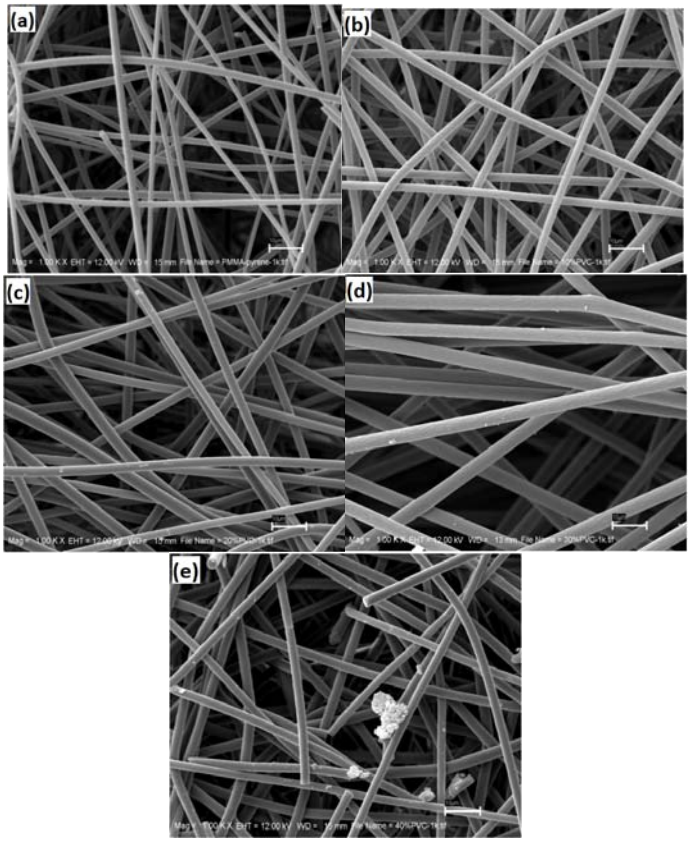
The intrinsic viscosity, [η], can be related to the molecular weight (M) of a linear polymer by Mark-Houwink-Sakurada equation:

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

where K and a are Mark-Houwink parameters. The critical chain overlap concentration, c*, of 120k PMMA solution in DMF at 25 °C was calculated by the criteria c* ~1/ [η], and found to be 2.8 wt.% using K and a values reported in the literature (K = 0.015 cm^3/g and a = 0.667). Previous study by Gupta et al. showed that uniform fibers were observed at c/c* ~10 for broad molecular weight distribution PMMAs. In this study, electrospinning of 30 wt.% PMMA solutions with c/c* of 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 Fig. 1, and fiber diameter distributions were shown in Fig. 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. At low PVC terpolymer contents, i.e. 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 obtain optimal electrospinning conditions, voltage and working distance were varied from 13.0-18.0 kV and 10-20 cm, respectively. SEM images of fibers obtained with these conditions were shown in Fig. 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.

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



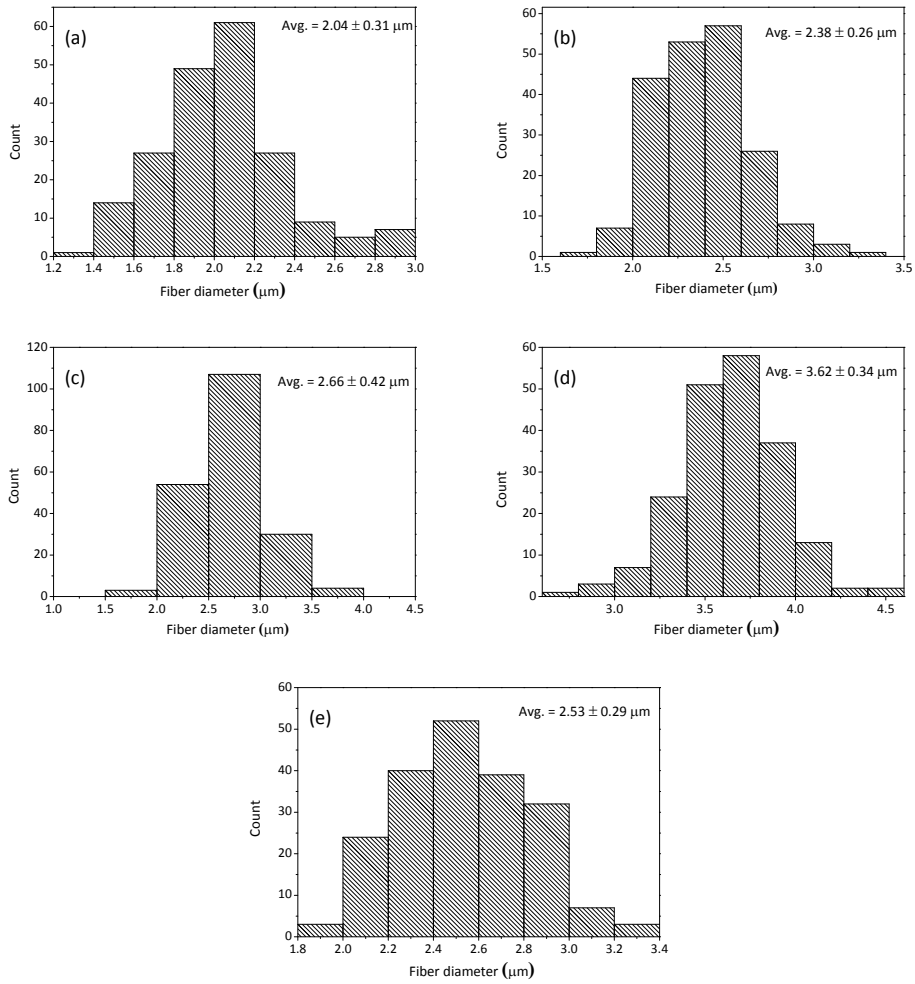
Sensing performance

UV–vis absorption spectrum of pyrene solution in Fig. 4 illustrated strong sharp bands at 308, 319 and 336 nm, corresponding to three vibrational sub-bands of single electron transfer ($S_0 \rightarrow S_2$). Emission spectra of pyrene solution and pyrene-doped fibers with 30% PVC terpolymer were also shown in Fig. 4. The maximum emission at 465 nm could be related to pyrene excimers, i.e. pyrene dimers or higher aggregates. 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 Fig. 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). 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% was selected for further studies due to the high fluorescence intensity of the excimer peak.

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



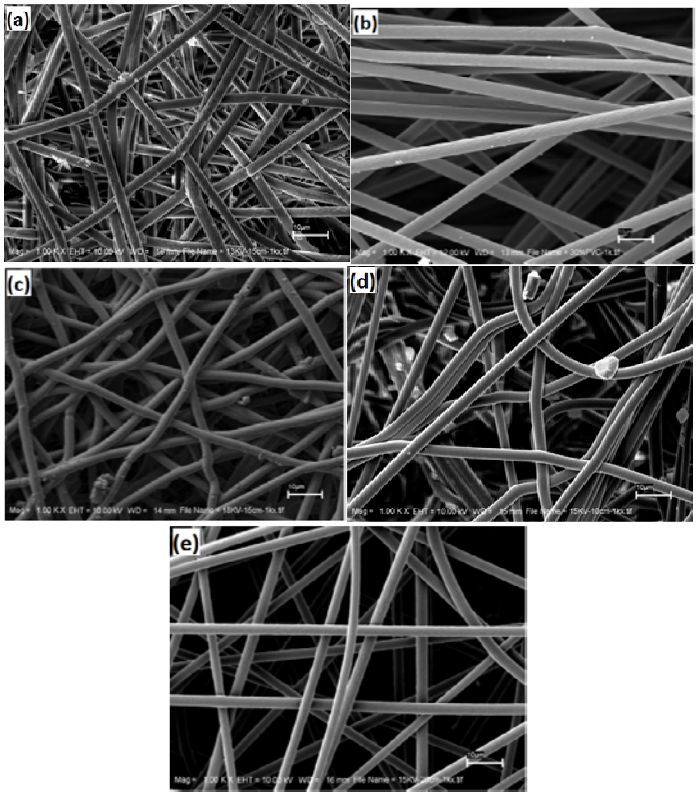
Fluorescence quenching can be described by Stern-Volmer equation

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

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 photo-induced electron transfer mechanism and/or electronic energy transfer. Fig. 6(a) showed a change of fluorescence 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 Fig. 6(b). K_{sv} calculated from the slope of the plot was 2.26×10^2 M^{-1}.

Figure 3. SEM images (1k 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. (Scale bar: 10 μm)



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. Fig. 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. Fig. 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). (λ_{Ex} = 336 nm).

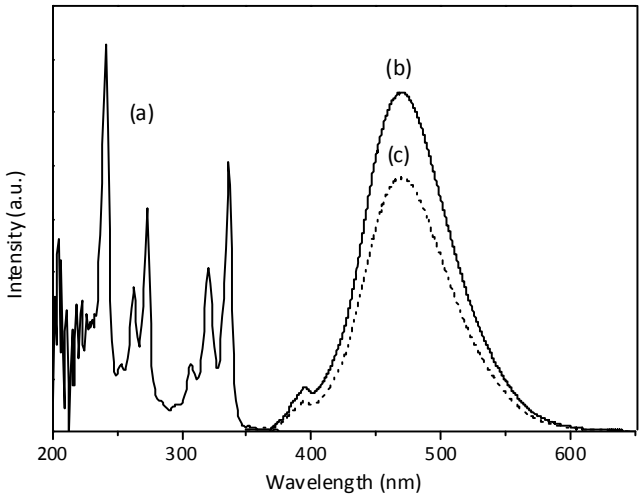


Figure 5. Emission spectra of PMMA/30%PVC fibers with various pyrene contents. (λ_{Ex} = 336 nm).

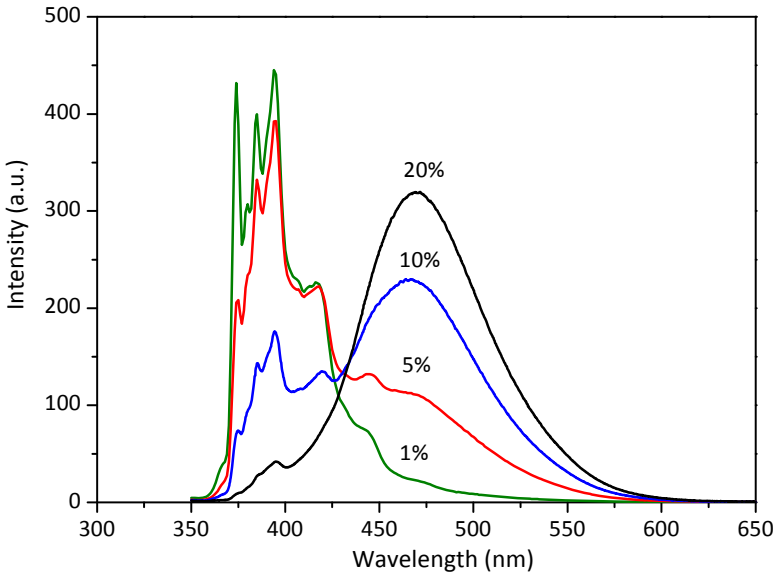


Figure 6. (a) Fluorescence spectra change of fibers with 30% PVC terpolymer and 20% pyrene as a function of Fe^{3+} concentration; [Fe^{3+}] = 0-5.0 mM (from top to bottom). (b) Stern-Volmer plot of the electrospun fibers in response to Fe^{3+}. (λ_{Ex}/ λ_{Em} = 336/465 nm).

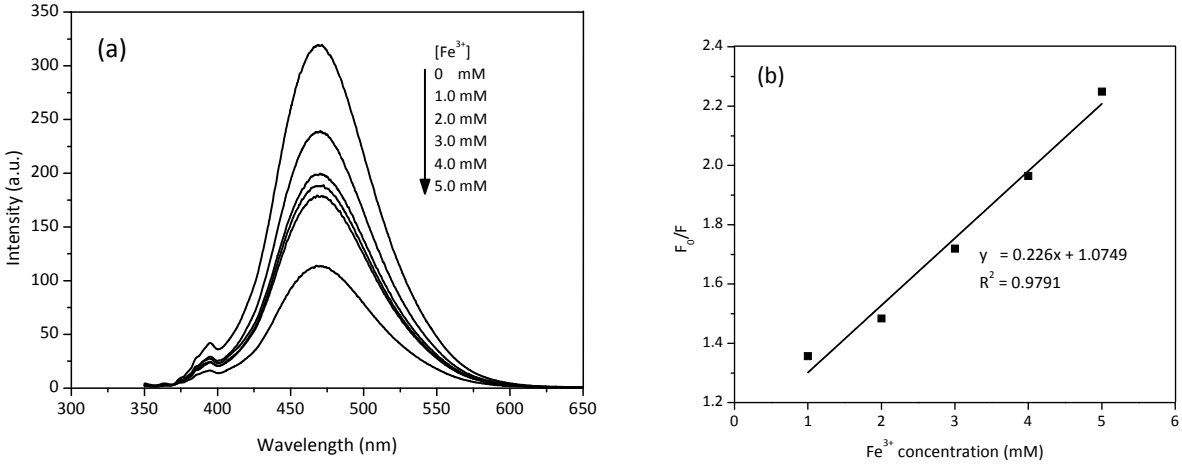


Figure 7. Responses of electrospun fibers to 1.0 mM solutions of various metal cations. (λ_{Ex}/ λ_{Em} = 336/465 nm).

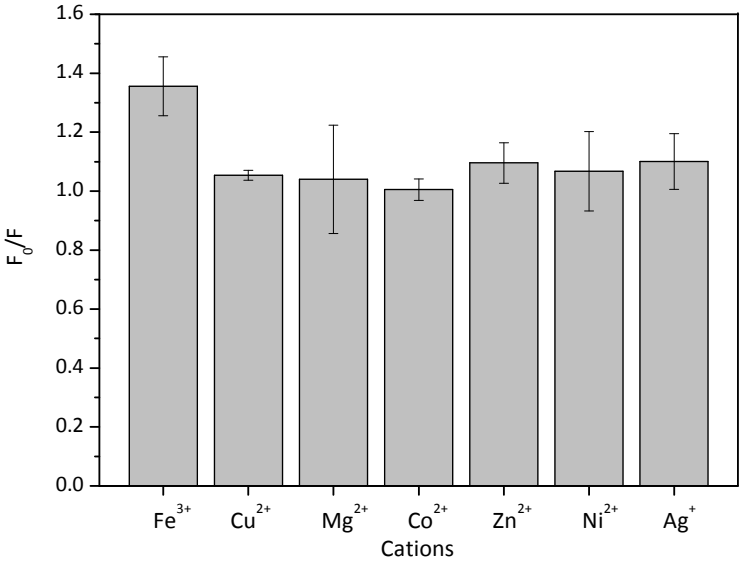
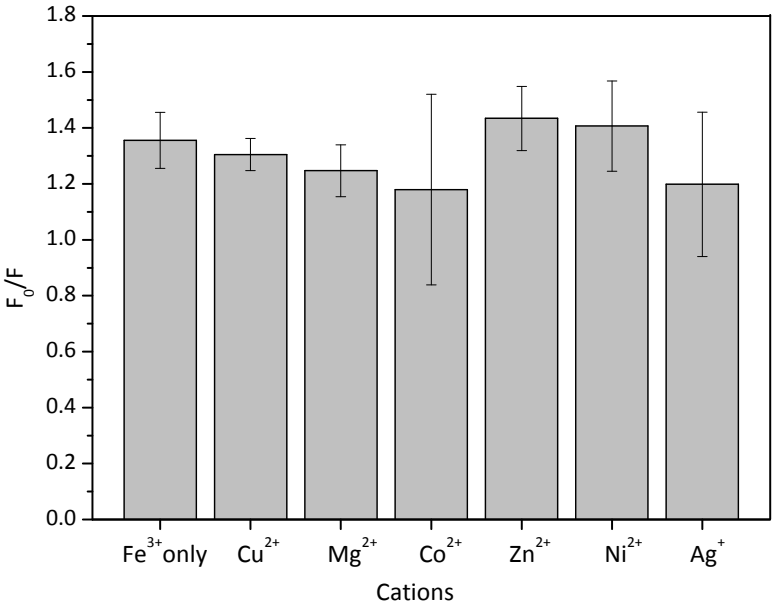


Figure 8. Quenching efficiency of fibers after being immersed into aqueous solution of Fe^{3+} (1.0 mM) only, and aqueous solution containing both Fe^{3+} (1.0 mM) and Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Ag^{+} (1.0 mM). (λ_{Ex}/ λ_{Em} = 336/465 nm).



6. Conclusion

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 0–40%, 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 x 10^2 M^{-1}. 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+}.

7. Appendix -

2. Enhancing performance of optical sensor through the introduction of polystyrene and porous structures

1. Abstract

Simple and promising approaches for developing high-performance Fe^{3+} sensors were proposed. Polyvinyl chloride (PVC) membrane containing pyrene as a fluorescent indicator was prepared via solvent-cast method. Upon immersion into 1.0 mM Fe^{3+} solution, the fluorescence emission of the membrane decreased with the ratio of fluorescence intensities before and after (F_0/F) immersion of 1.25. The sensitivity enhancement was achieved through the introduction of polystyrene (PS) onto PVC and the introduction of porous structures. Polyvinyl chloride-*graft*-polystyrene copolymers (PVC-*g*-PS) were synthesized via Atom Transfer Radical Polymerization (ATRP) using PVC as macroinitiator. The grafting percentages of PS on PVC calculated from Nuclear Magnetic Resonance Spectroscopy (NMR) were 17 and 41. The membrane prepared from low molecular weight copolymer showed higher sensing ability than that from PVC with the F_0/F value of 1.39. The increase in PS chain length did not significantly affect the fluorescence quenching. A Stern–Volmer quenching relationship was found with K_{sv} of 3.96 x 10^2 M^{-1}. The effect of porous structures on fluorescence quenching was studied by introducing Triton X-100 as a porogen to PVC/pyrene solution. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and Scanning Electron Microscopy (SEM) analyses confirmed a complete removal of Triton X-100 after 3 days of immersion in water. The porous membrane demonstrated an enhanced sensing performance with the F_0/F value of 1.46. PVC-*g*-PS/pyrene membrane exhibited highly sensitive and selective responses toward Fe^{3+} over Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Ag^{+}. In addition, a good reversibility after five cycles of quenching and regeneration was obtained.

2. Executive summary

In this work, fluorescence quenching-based sensing membranes for Fe^{3+} detection were prepared from solution of PVC and pyrene via solvent-cast method. Two approaches were carried out in order to improve the performance of the sensor. The first approach was to introduce polystyrene onto PVC. Polyvinyl chloride-*graft*-polystyrene (PVC-*g*-PS) was synthesized via atom transfer radical polymerization (ATRP) using PVC as macroinitiator. Sensing performance of pyrene-doped membranes prepared from PVC graft copolymer was compared with that from PVC homopolymer. The effect of PS chain length on fluorescence quenching was also studied. The second approach was to introduce porous structures to PVC and PVC-*g*-PS membranes using Triton X-100 as a porogen. The effect of membrane porosity on quenching was investigated. The sensitivity and selectivity toward Fe^{3+} and other metal ions, and the reusability of the prepared membranes were discussed.

3. Objective

To prepare PVC-based membranes as sensing materials for Fe^{3+}

4. Research methodology

Materials

Polyvinyl chloride (PVC, M_W 43,000, M_n 22,000), styrene (>99%), pyrene (>98%), aluminum oxide (basic), copper (I) bromide (CuBr, >98%), iron (III) nitrate nonahydrate, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, >99%), and 1-methyl-2-pyrrolidinone (NMP, 99%) were purchased from Sigma-Aldrich (U.S.A.). Triton X-100 was obtained from Merck (U.S.A). Magnesium (II) sulfate heptahydrate, zinc chloride and silver nitrate were supplied by Carlo Erba Reagents (Thailand). Nickel (II) sulfate hexahydrate and cobalt (II) nitrate hexahydrate were purchased from Guangdong Guanghua Chemical Factory Co. Ltd (China). Copper (II) nitrate hemipentahydrate and ethylenediaminetetraacetic acid disodium salt (Na_2EDTA, 99%) were obtained from Ajax Finechem (Thailand). All chemicals were used as received.

Synthesis of Polyvinyl Chloride-*Graft*-Polystyrene

PVC-*g*-PS was synthesized via ATRP and the procedures were as follows: PVC (5.0007 g) was dissolved in NMP (40.0 mL) in a round bottom flask at room temperature for 5 h. Styrene was purified by passing through a short column of basic alumina. Styrene (10.0135 g), PMDETA (290 μL, 1.39 mmol) and CuBr (0.2004 g, 1.39 mmol) were then added to PVC solution. The solution was flushed with N_2 for 15 min, and then stirred at 90 °C for 7 h. After polymerization, the residual copper catalyst was removed by passing the reaction mixture down a short column filled with basic alumina. The polymer solution was concentrated and precipitated in methanol. In the synthesis of PVC-*g*-PS with higher molecular weight, the amounts of PMDETA and CuBr were doubled.

Membrane Preparation

A 5 wt.% polymer (PVC or PVC-*g*-PS) solution was prepared by dissolving polymer and pyrene (20% by weight of polymer) in tetrahydrofuran (THF). The solution was stirred for 24 h prior to casting on a petri dish. The membrane was dried at room temperature, and later peeled off. In a preparation of porous membrane, Triton X-100 was added to polymer/pyrene solution prior to stirring for 24 h. The weight ratio of polymer and Triton X-100 was 1/1. The solvent-cast membrane was dried at room temperature, and later peeled off. Due to the water solubility of Triton X-100, it was consequently washed away from the membrane by immersing in deionized (DI) water with a shaking speed of 120 rpm.

Characterization

^{1}H-NMR (400 MHz) spectra were obtained on a Varian Mercury-400 NMR Spectrometer with the samples dissolved in chloroform-d containing tetramethylsilane (TMS). Molecular weight was measured by Gel Permeation Chromatography (GPC) in THF at 40 °C with a flow rate of 1.0 mL/min on a system equipped with Styragel HR5E column, and refractive index detector (waters 2414). Polystyrene standards were used for molecular weight calibration. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were measured on a Bruker FTIR spectrometer (Tensor 27) with Opus 7.0 software. Emission spectra were recorded using an RF-5301PC spectrofluorophotometer (Shimadzu) with excitation/emission slit widths of 3/5 nm (low sensitivity) for PVC/pyrene and PVC/pyrene/Triton X-100 membranes, 1.5/3 nm (high sensitivity) for low molecular weight PVC-*g*-PS/pyrene membrane, 3/1.5 nm (high sensitivity) for high molecular weight PVC-*g*-PS/pyrene membrane, and 5/5 nm (low sensitivity) for PVC-*g*-PS/pyrene/Triton X-100 membranes. Membranes were gold-coated prior to imaging by a Scanning Electron Microscope (SEM, SEC Co., Ltd., SNE-4500M). The average pore sizes were determined from 200 pore diameters in each micrograph using WCIF ImageJ program.

Sensitivity Study

Response performance of membranes toward Fe^{3+} ions was carried out as follows. The membranes were cut into 1 cm x 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 emissions at 470, 483, and 485 nm (F_0) were recorded for PVC, low molecular weight PVC-*g*-PS, and high molecular weight PVC-*g*-PS, respectively. The membranes were then immersed into 1.0 mM aqueous ferric nitrate solution for 30 minutes. After thorough washing with water, the membranes were dried prior to fluorescence emission measurements (F). The mean of three fluorescence emission measurements was used for each sample, and the reported F_0/F value was the mean of two replicates. In a study of the effect of Fe^{3+} concentration on fluorescence quenching, high molecular weight PVC-*g*-PS/pyrene membrane was immersed into ferric nitrate solutions of different concentrations ranging from 0 to 1.0 mM.

Selectivity and Interference Studies

To investigate the selectivity of the membrane prepared from low molecular weight PVC-*g*-PS 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 selected metal ion (1.0 mM) were used in interference study.

Reusability Study

The reusability study was conducted as follows. After immersing PVC-*g*-PS membrane into 1.0 mM Fe^{3+} solution for 30 minutes, the membrane was washed with water, and later immersed into the saturated Na_2EDTA solution for 30 minutes. The membrane was washed with water, and dried prior to fluorescence emission measurements.

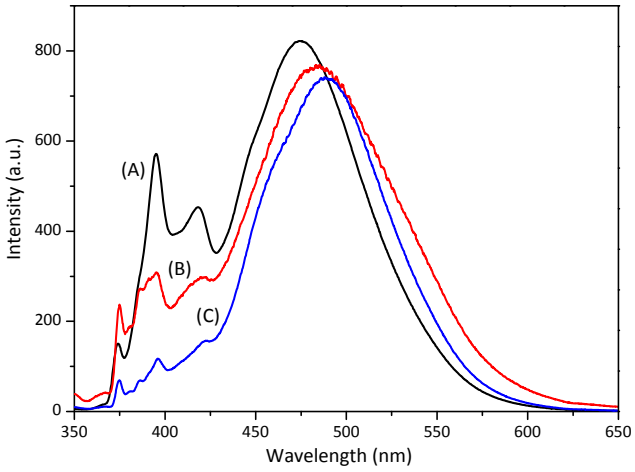
5. Results and discussions

PVC/Pyrene Membrane

Membrane Preparation and Emission Spectrum

Free standing membrane with a thickness of 0.21 mm was obtained from PVC/pyrene solution. Emission spectrum of pyrene-doped PVC membrane was shown in Figure 1(A). The two major bands between 370 nm and 420 nm and centered at 470 nm could be ascribed to the emission from excited pyrene monomer, and pyrene excimer, respectively.

Figure 1. Emission spectra of PVC/pyrene membrane (A), low molecular weight PVC-*g*-PS/pyrene membrane (B), and high molecular weight PVC-*g*-PS/pyrene membrane (C).



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 470 nm of pyrene-doped PVC membrane before and after immersion in 1.0 mM Fe^{3+} solution (F_0/F) for 30 minutes was 1.25. The fluorescence quenching could be due to

interactions of electron-rich dye, pyrene, and electron-deficient quencher, Fe^{3+}, via a photo-induced electron transfer mechanism (PET) and/or electronic energy transfer.

Effect of Immersion Period in Fe^{3+} Solution on Quenching

Another piece of the prepared membrane was immersed into 1.0 mM Fe^{3+} solution for 90 minutes. The average F_0/F value was found to be 1.21. Since there was no significant difference in fluorescence quenching between using the immersion periods of 30 and 90 minutes, the immersion period of 30 minutes was selected for sensing performance studies.

PVC-*g*-PS/Pyrene Membranes: Effects of Polymeric Matrix and PS Chain Length on Quenching

PVC-g-PS Synthesis

Polyvinyl chloride-*graft*-polystyrene was synthesized via ATRP using PVC as macroinitiator and CuBr/PMDETA catalyst system. PVC-*g*-PS copolymers with two different PS chain lengths were obtained by varying the amounts of CuBr and PMDETA. The synthetic scheme was shown in Scheme 1. Successful synthesis was confirmed by ^{1}H-NMR spectra in Figure 2. The peaks around 4.5 ppm corresponded to CHCl of PVC. Upon grafting PS onto PVC, two additional peaks around 6.5 and 7.1 ppm were shown. The grafting percentage was calculated from the integrals of peaks from PS at 6.5 and 7.1 ppm, and that from PVC at 4.5 ppm. Grafting percentages of PS onto PVC of the two polymers were 17 and 41.

The number-average molecular weights and polydispersity indices (PDI) obtained from GPC of the two PVC-*g*-PS copolymers were 32,100 (PDI 2.38), and 69,800 (PDI 2.22). A unimodal GPC peak with a small increase in PDI compared to that of PVC homopolymer suggested that there was no homopolymer contamination or coupling reactions.

Scheme 1. Synthesis of PVC-*g*-PS via ATRP.

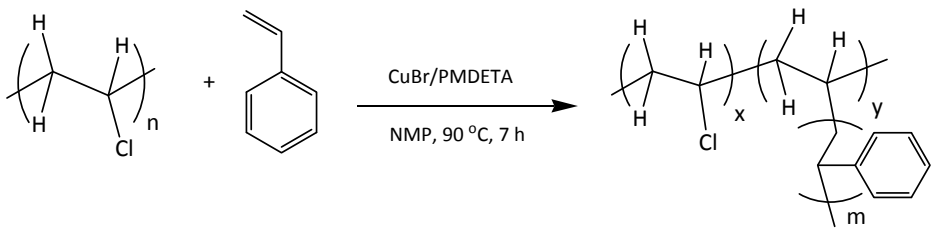
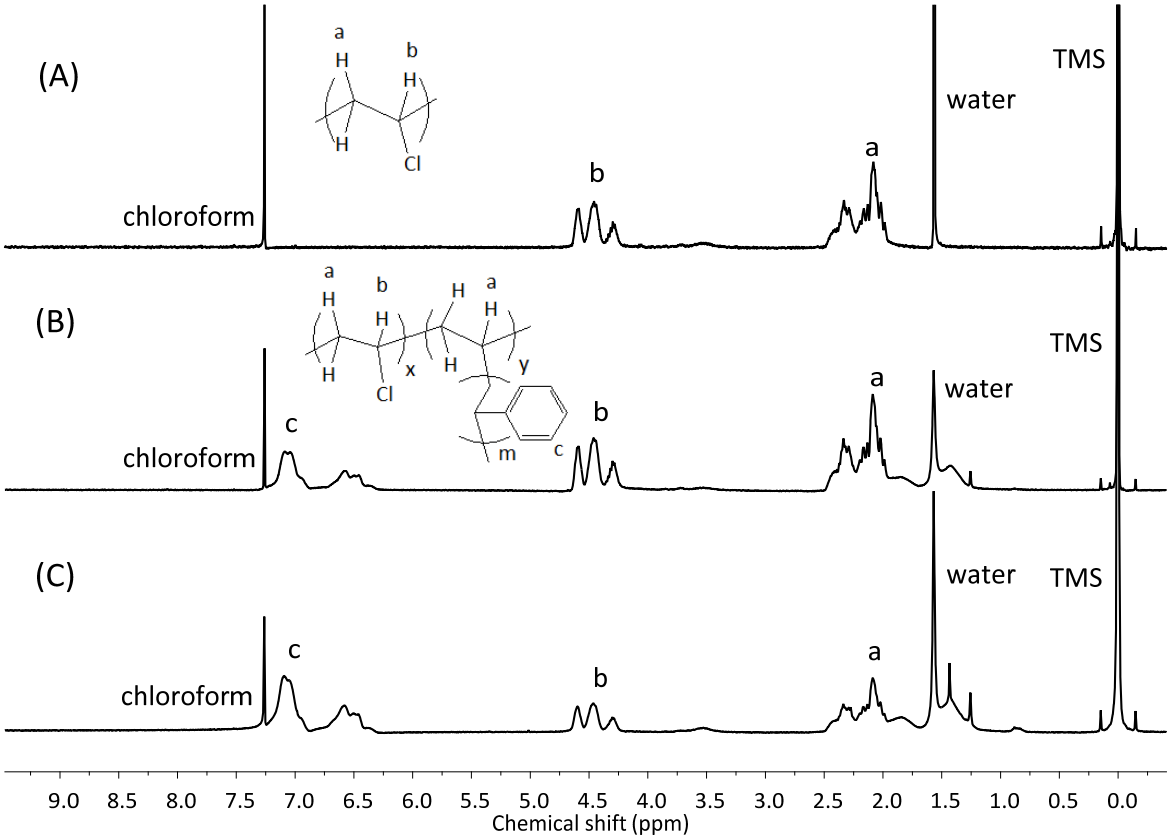


Figure 2. NMR spectra of PVC (A), low molecular weight PVC-*g*-PS (B), and high molecular weight PVC-*g*-PS (C).



Sensing Performance of PVC-g-PS/Pyrene Membranes

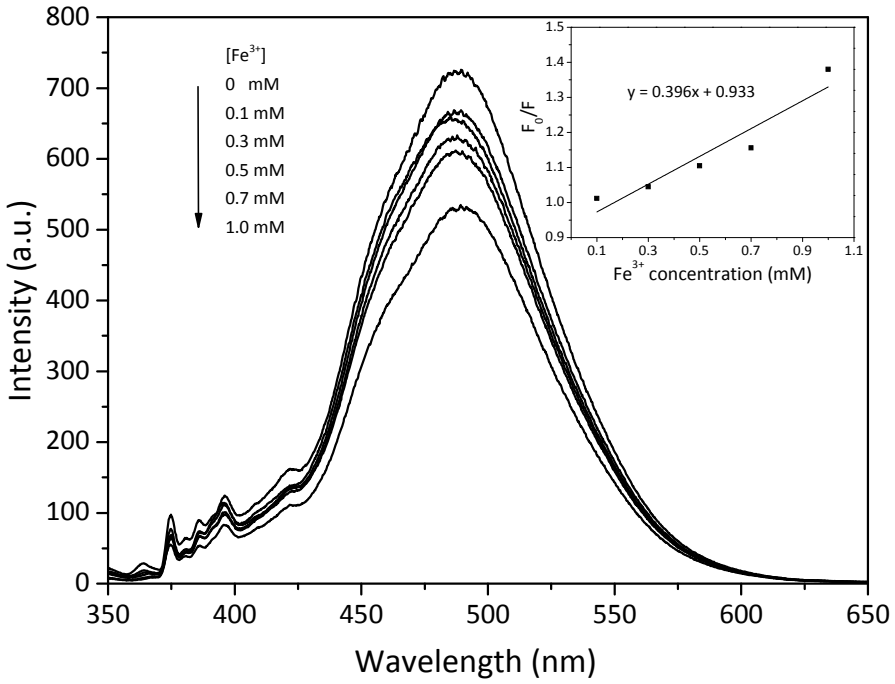
The emission spectrum of low molecular weight PVC-*g*-PS/pyrene membrane in Figure 1(B) showed a red shift of the excimer emission relative to that of PVC/pyrene membrane by 13 nm to 483 nm, indicating a formation of pyrene aggregation. It was also found that as PS chain length was increased, the excimer emission was further shifted to a longer wavelength.

Sensing performances toward 1.0 mM Fe^{3+} solution of membranes prepared from the two graft copolymers were compared with that from PVC. PVC-*g*-PS membranes showed higher sensing abilities with F_0/F values of 1.39 and 1.38 for low molecular weight and high molecular weight, respectively. The pronounced sensitivity could possibly be due to the co-facial π-π stacking between the phenyl side chains of PS and pyrene ("molecular wire" amplification). The π conjugated system increases the possibility of interaction between pyrene and Fe^{3+}, leading to high fluorescence quenching. The enhancement in sensing performance through enlarging the effective conjugation degree of π system has also been observed in other pyrene-based fluorescent sensors. No drastic change in quenching ability was observed when PS chain was extended. Despite a much lower

surface area, which could be 1 to 2 orders of magnitudes lower, these continuous pyrene-doped PVC-*g*-PS membranes showed comparable Fe^{3+} response performance to our micron-size fibers from poly(methyl methacrylate), poly(vinyl chloride-*co*-vinyl acetate-*co*-vinyl alcohol) and pyrene.

The effect of Fe^{3+} concentration on fluorescence intensity of high molecular weight PVC-*g*-PS/pyrene membrane was shown in Figure 3. The intensity was found to gradually decrease with increasing Fe^{3+} concentration. A linear plot between Fe^{3+} concentration and F_0/F provided a K_{sv} value of 3.96 x 10^2 M^{-1}.

Figure 3. Fluorescence spectra change of high molecular weight PVC-*g*-PS/pyrene membrane as a function of Fe^{3+} concentration; [Fe^{3+}] = 0 - 1.0 mM (from top to bottom) and corresponding Stern-Volmer plot (inset). (λ_{Ex}/ λ_{Em} = 336/485 nm).



PVC/Pyrene/Triton X-100 Membranes: Effect of Porosity on Quenching

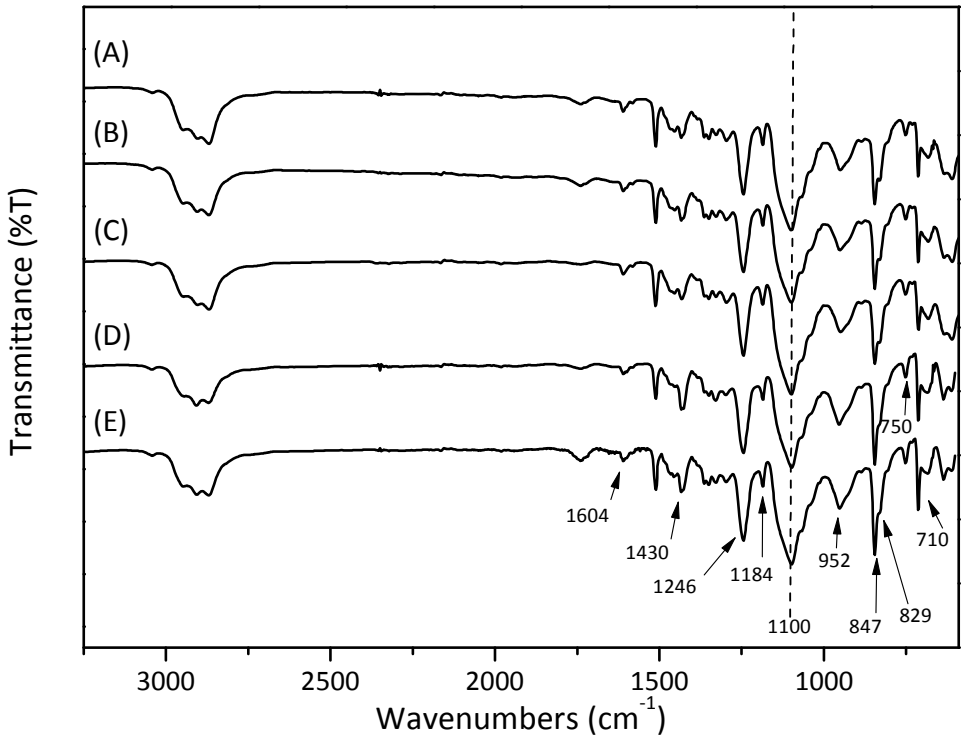
Preparation of Porous PVC Membrane

Another approach to improve the sensing performance of PVC/pyrene membrane was conducted through the introduction of porous structures using Triton X-100 as a water-soluble porogen. ATR-FTIR spectra of PVC/pyrene/Triton X-100 membranes before and after immersion in water were shown in Figure 4. Characteristic bands of PVC at 1,246, 952 and 847 cm^{-1} were assigned to C-H rocking, C-H wagging, and C-Cl stretching, respectively. The band corresponding to C-C stretching was also present at 1,096 cm^{-1}. The bands at 1,604, 1,430 and 829 cm^{-1} of pyrene

were assigned to C=C stretchings and bands at 1,184, 750 and 710 cm^{-1} were assigned to three adjacent C-H stretchings. The band relating to C-O stretching of Triton X-100 was shown at 1,100 cm^{-1}, overlapping with the C-C stretching band of PVC. A decrease of band intensity at 1,100 cm^{-1} suggested a complete removal of Triton X-100 after 3 days of immersion in water.

SEM images of pyrene-doped PVC/Triton X-100 membranes before and after immersion in water for 1, 2, 3, and 4 days were shown in Figure 5. Similar pore sizes were observed after 3 and 4 days of immersion, suggesting that Triton X-100 was completely removed after 3 days. Since FTIR results had good agreement with SEM analysis, immersion in water for 3 days was chosen for further investigations.

Figure 4. ATR-FTIR spectra of PVC/pyrene membrane containing Triton X-100 before (A) and after immersion in water for 1 day (B), 2 days (C), 3 days (D), and 4 days (E).

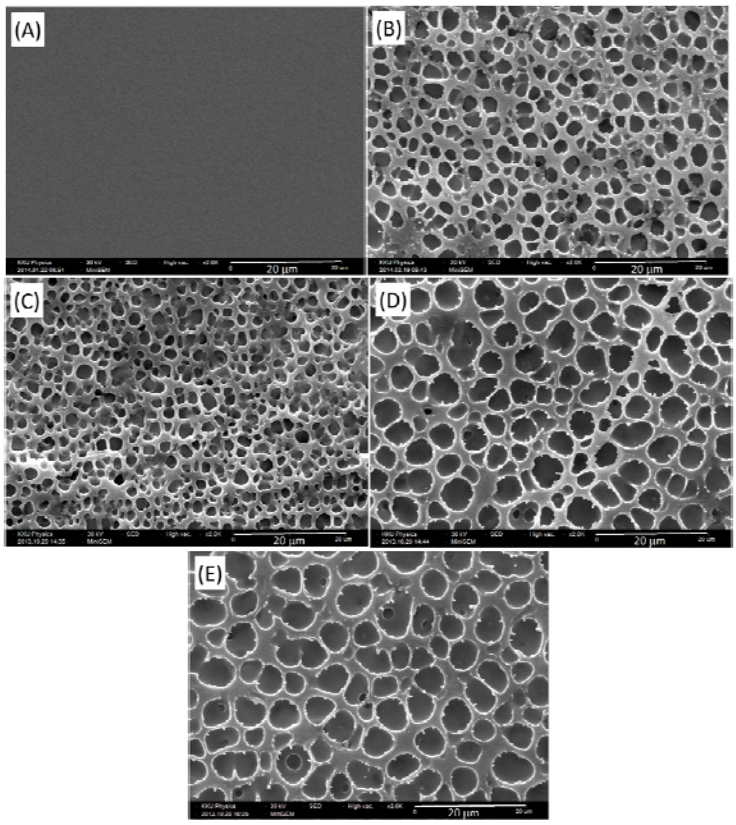


Sensing Performance of Porous PVC/Pyrene Membrane

Prior to Fe^{3+} sensing study, fluorescence emissions of PVC/pyrene/Triton X-100 membranes before and after immersion in water for 3 days were compared. Similar fluorescence intensities suggested that there was no pyrene leakage during Triton X-100 removal. Sensing performance of PVC membrane with porous structures was then evaluated. The higher F_0/F value of 1.46 of the

porous membrane is likely attributed to the increased surface area which provides faster diffusion of the quencher to the sensing elements.

Figure 5. SEM images (2k magnification) of PVC/pyrene/Triton X-100 membranes before (A) and after immersion in water for 1 day (B), 2 days (C), 3 days (D), and 4 days (E). The average pore sizes of (B), (C), (D), and (E) were 2.25 ± 0.70, 2.51 ± 0.63, 4.13 ± 1.31, and 4.92 ± 1.60, respectively. Scale bar is 20 μm.

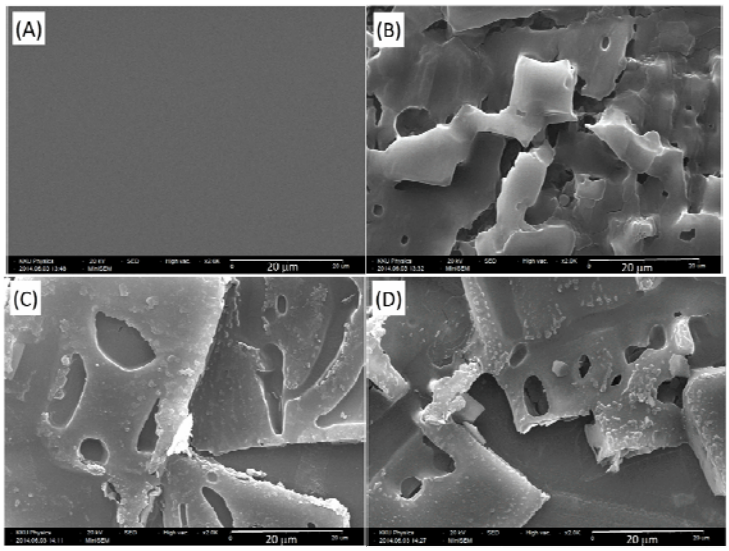


PVC-*g*-PS/Pyrene/Triton X-100 Membranes: Effect of Both PS and Porosity on Quenching

Preparation and Sensing Performance of Porous PVC-g-PS/Pyrene Membranes

The effect of both PS incorporation and porous structures on fluorescence quenching was further explored. Porous PVC-*g*-PS membrane was prepared as described for porous PVC membrane. Figure 6 displayed SEM images of the membranes before and after immersion in water for 3, 4, and 5 days. Rough surfaces with non-uniform pores were observed after being immersed in water. FTIR results (data not shown) suggested a complete removal of Triton X-100 after 3 days of immersion. The fluorescence quenching ability of this porous membrane was investigated. A relatively low sensing performance with the F_0/F value of 1.21 could possibly be due to a reduction in number of small pores, i.e. a decrease in surface area, and a decrease in long-range exciton migration between PS and pyrene created from non-uniform porous structures.

Figure 6. SEM images (2k magnification) of PVC-*g*-PS/pyrene/Triton X-100 membranes before (A) and after immersion in water for 3 days (B), 4 days (C), and 5 days (D). Scale bar is 20 μm.



Selectivity and Interference Studies of PVC-*g*-PS/pyrene Membranes

Although a large number of porous structures in PVC/pyrene membrane offered such a high sensitivity, they also made the membrane more brittle. Therefore, the PVC-*g*-PS/pyrene membrane was chosen for selectivity and interference studies.

The selectivity of the sensing membrane prepared from low molecular weight PVC-*g*-PS was evaluated by immersing the membrane into 1.0 mM aqueous solutions of Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Ag^{+}. Figure 7 revealed that the membrane was 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 1.39, 1.06, 1.04, 1.00, 1.07, 1.07 and 1.04, respectively. The interference effect of other metal ions on quenching ability of Fe^{3+} was also studied. Similar F_0/F values in Figure 8 indicated that the binding of Fe^{3+} to pyrene was not interrupted by the presence of other selected ions.

Reusability Study

The low molecular weight PVC-*g*-PS membrane was alternately exposed to 1.0 mM Fe^{3+} solution and saturated Na_2EDTA solution. The corresponding fluorescence emission was measured. As shown in Figure 9, the membrane showed good reversibility with less than 22% signal loss after 5 cycles of quenching and regeneration. Since Fe^{3+} forms a stronger complex with Na_2EDTA than with pyrene, the reversibility could be obtained.

Figure 7. Responses of PVC-*g*-PS membranes to 1.0 mM solutions of various metal cations. (λ_{Ex}/ λ_{Em} = 336/483 nm).

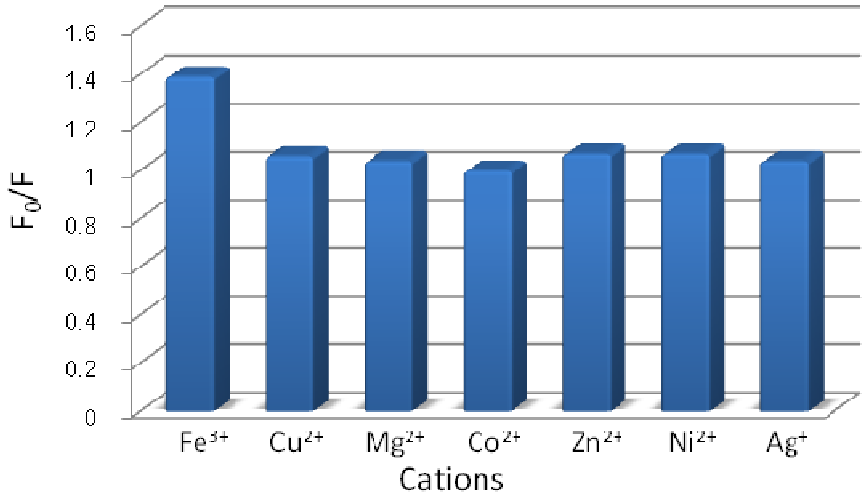


Figure 8. Quenching efficiencies of PVC-*g*-PS membranes after being immersed into solution of Fe^{3+} (1.0 mM) only, and solutions containing both Fe^{3+} (1.0 mM) and other metal ion (1.0 mM). (λ_{Ex}/ λ_{Em} = 336/483 nm).

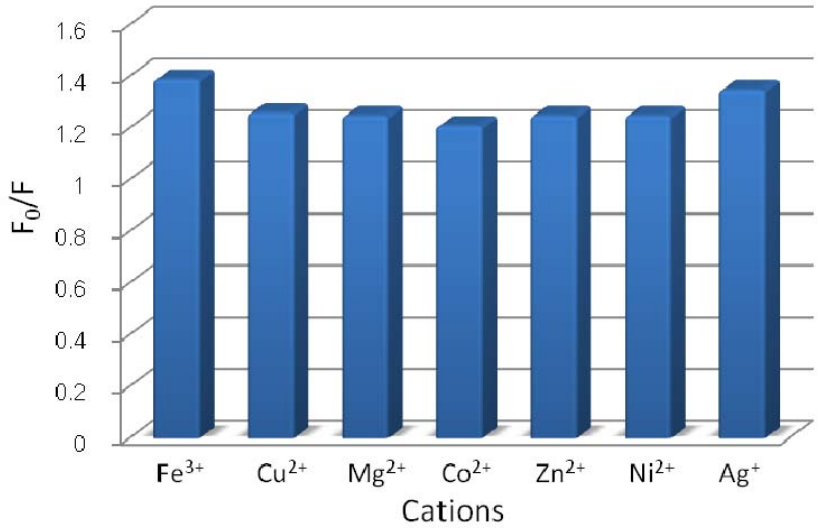
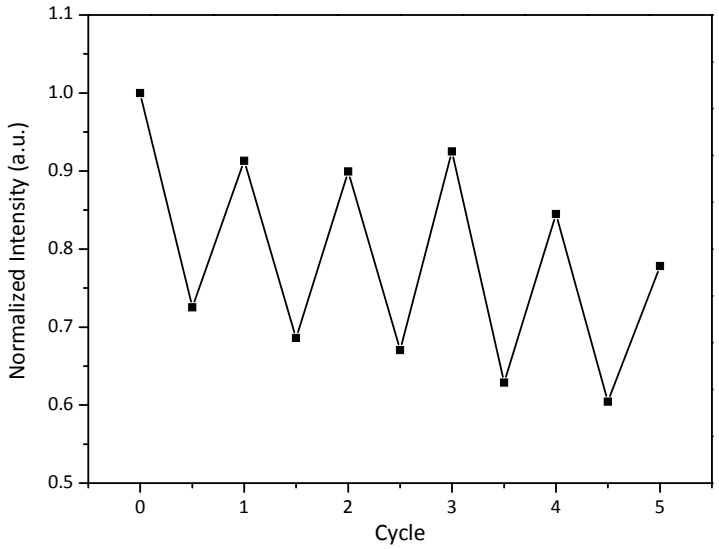


Figure 9. Fluorescence intensities of PVC-*g*-PS membrane after alternate treatment by solutions of Fe^{3+} and Na_2EDTA. ($\lambda_{Ex}/\lambda_{Em}$ = 336/483 nm).



6. Conclusion

This work provides simple and efficient approaches to fabricate fluorescence quenching-based optical sensor for Fe^{3+} detection. Self-standing pyrene-doped PVC membrane was prepared via solvent-cast method. The sensitivity was enhanced through the introduction of PS onto PVC via ATRP and the introduction of porous structures using Triton X-100 as a porogen. PS chain length did not significantly affect the quenching ability of the membrane. The ratios of fluorescence intensities of low molecular weight PVC-*g*-PS membrane and porous PVC membrane before and after (F_0/F) immersion in Fe^{3+} solution were 1.39 and 1.46, respectively. Introductions of both PS and porous structures did not result in an improvement in sensing performance in this study. PVC-*g*-PS membrane exhibited highly sensitive and selective responses toward Fe^{3+} over other selected metal ions with good reusability.

7. Appendix –

8. Output (Acknowledge the Thailand Research Fund)

8.1 International Journal Publication

1. Martwiset S*, Nijpanich S, Banturngsaksiri A, Sriring M, Pandhumas T, Youngme S. Pyrene-doped electrospun PMMA-PVC fibers for ferric ion detection. Journal of Applied Polymer Science 2013; 130 (5): 3205-3211.

2. Panawong C, Pandhumas T, Youngme S, Martwiset S*. Enhancing performance of optical sensor through the introduction of polystyrene and porous structures. Journal of Applied Polymer Science 2015; 132 (14): 41759.

8.2 Application -

8.3 Others e.g. national journal publication, proceeding, international conference, book chapter, patent

1. Panawong C, Martwiset S*. Ferric ion sensor based on polyvinyl chloride and polyvinyl chloride-graft-polystyrene membranes. PACCON2014, January 8-10, 2014. Khon Kaen, Thailand. Poster presentation.

2. Panawong C, Pandhumas T, Martwiset S*. Effect of polystyrene incorporation on ferric ion detection. MACRO2014, 6-11 July 2014, Chiang mai, Thailand. Poster presentation.

Journal of Applied Polymer Science

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 m*M* Fe^{3+} solution was 1.36. The effect of Fe^{3+} concentrations (0–5.0 m*M*) on quenching ability was investigated. An excellent Stern–Volmer quenching relationship was found with K_{SV} of 2.26 × 10^2*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

KEYWORDS: electrospinning; fibers; sensors and actuators; dyes/pigments; poly(vinyl chloride)

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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 m*M* 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 m*M* 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 m*M*) and other metal ion (1.0 m*M*) 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 cm^3/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^* of 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

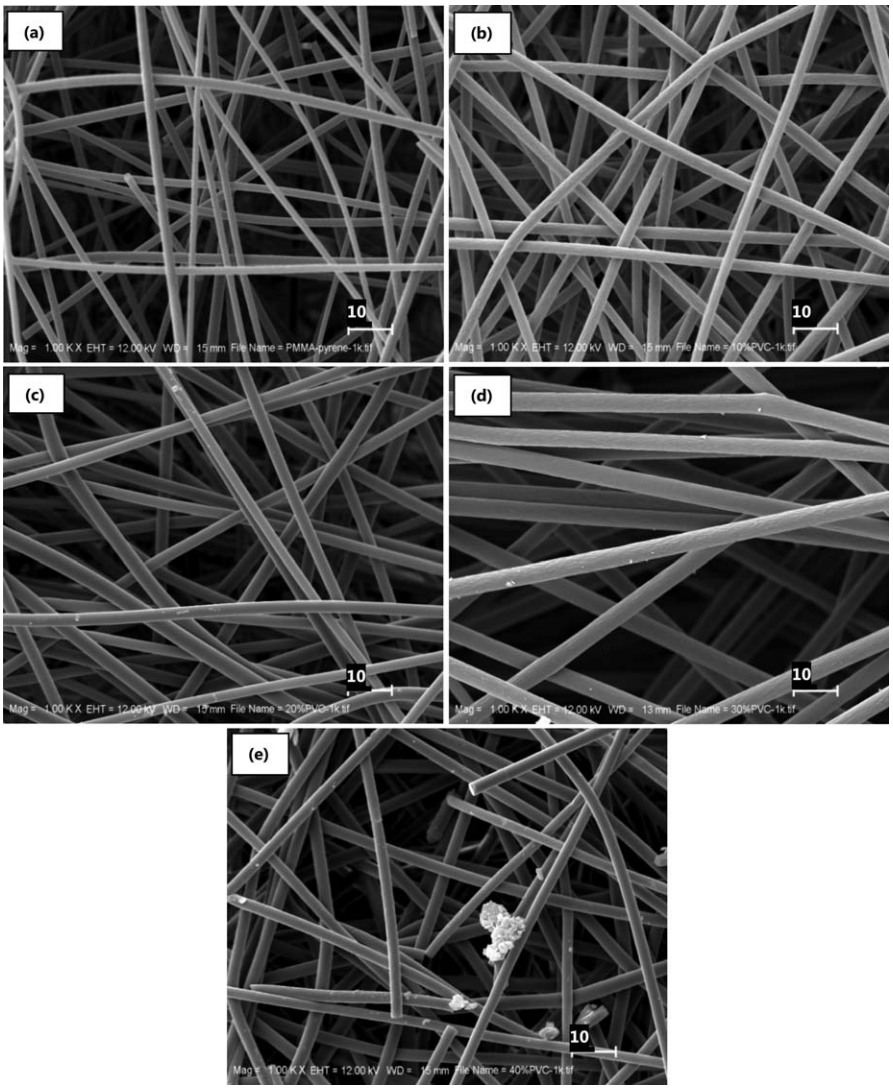

Figure 1. SEM images (1 k magnification) of electrospun fibers with various PVC terpolymer contents. (a) 0, (b) 10, (c) 20, (d) 30, and (e) 40%.

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 $\pm$ 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%

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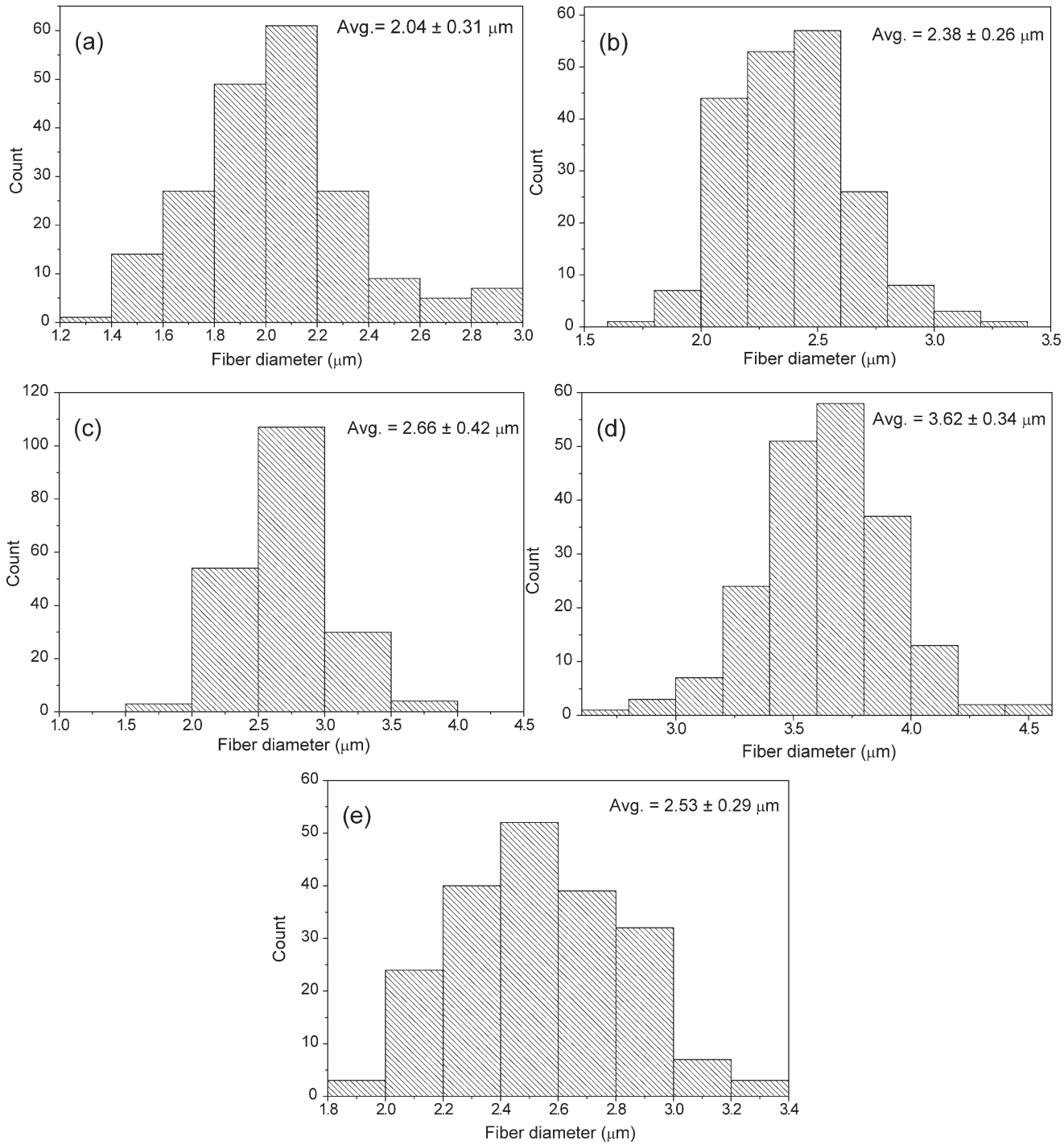

Figure 2. Size distributions of fibers with (a) 0, (b) 10, (c) 20, (d) 30, and (e) 40% PVC terpolymer.

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 m*M* 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

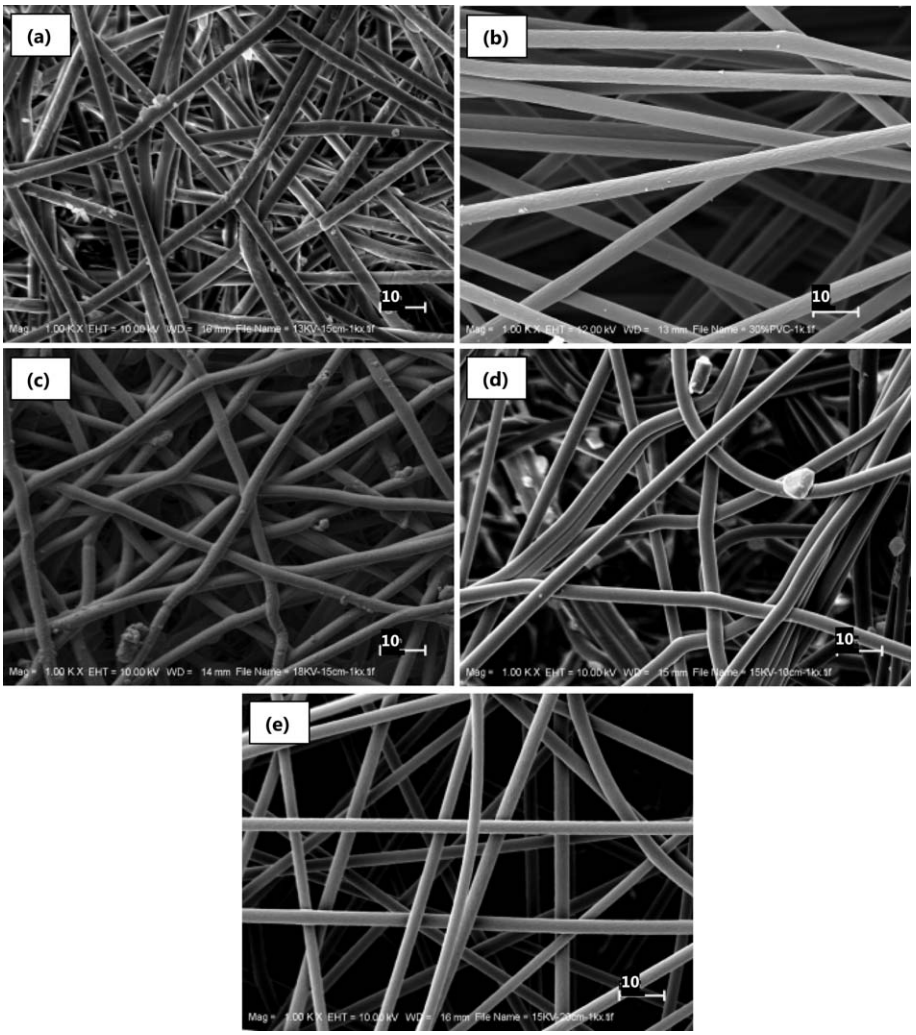

Figure 3. SEM images (1 k magnification) of fibers obtained with various electrospinning conditions. (a) 13.0 kV, 15 cm, (b) 15.0 kV, 15 cm, (c) 18.0 kV, 15 cm, (d) 15.0 kV, 10 cm, and (e) 15.0 kV, 20 cm.

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 m*M* 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.

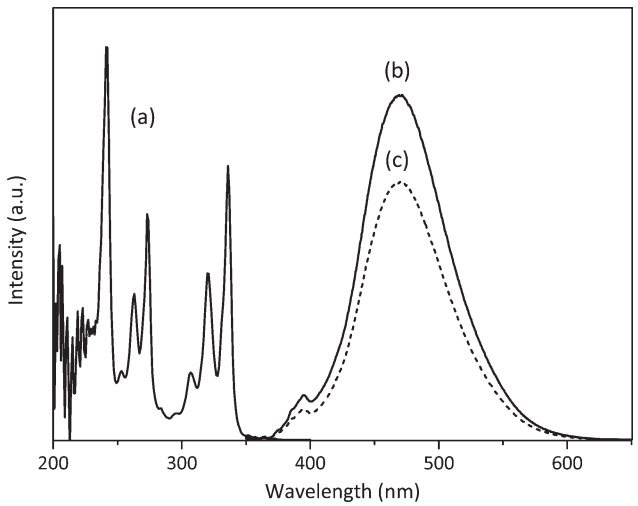

Figure 4. Absorption spectrum of pyrene in THF (a), emission spectrum of pyrene in chloroform (b), and emission spectrum of PMMA/pyrene/PVC fibers (c) (λ_{Ex} = 336 nm).

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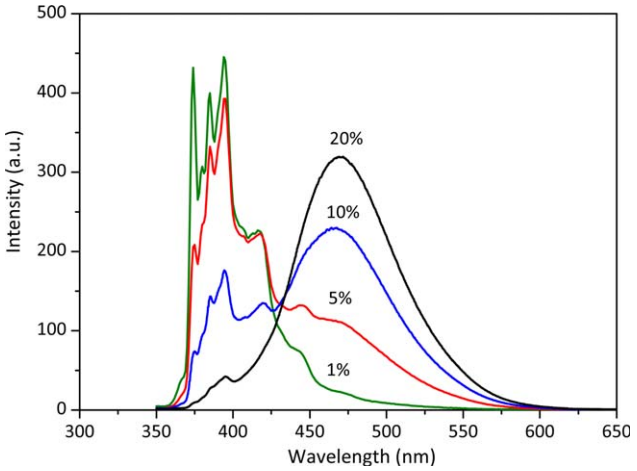

Figure 5. Emission spectra of PMMA/30% PVC fibers with various pyrene contents (λ_{Ex} = 336 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

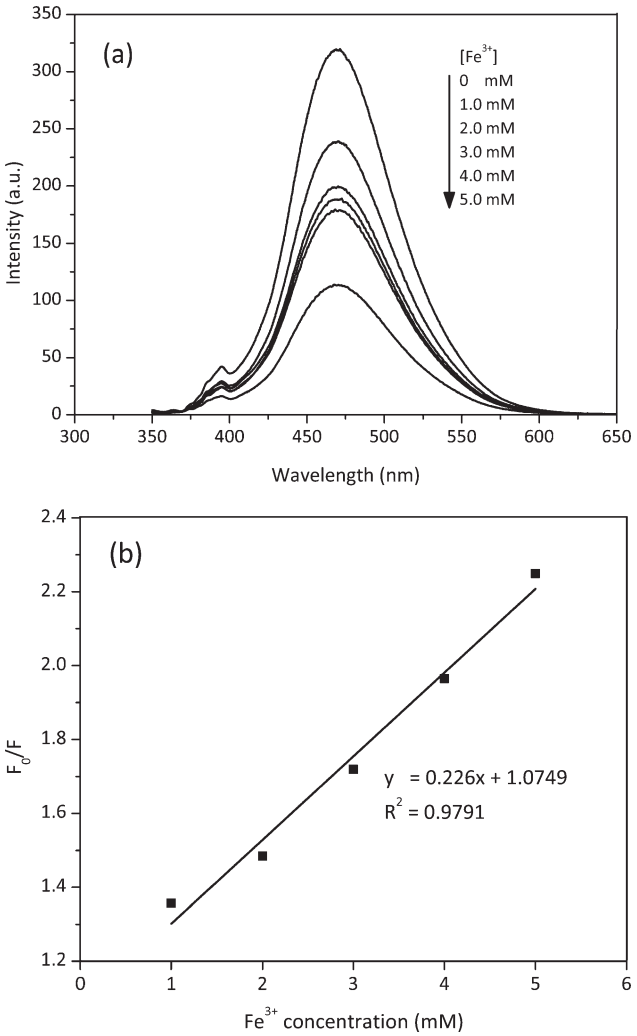

Figure 6. (a) Fluorescence spectra change of fibers with 30% PVC terpolymer and 20% pyrene as a function of Fe^{3+} concentration; [Fe^{3+}] = 0–5.0 m*M* (from top to bottom). (b) Stern-Volmer plot of the electrospun fibers in response to Fe^{3+}. ($\lambda_{Ex}/\lambda_{Em}$ = 336/465 nm).

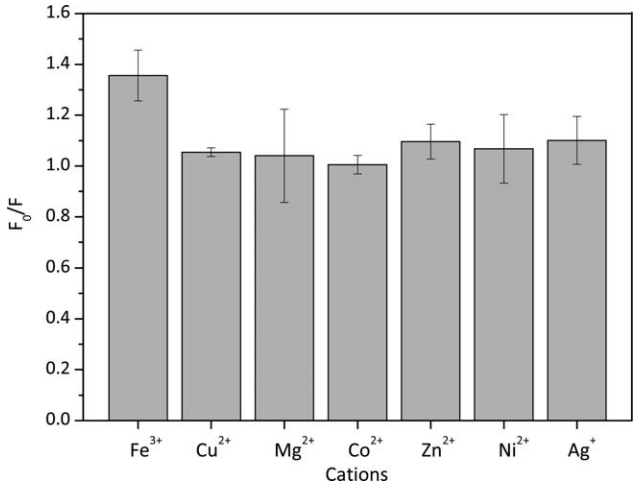

Figure 7. Responses of electrospun fibers to 1.0 m*M* solutions of various metal cations. ($\lambda_{Ex}/\lambda_{Em}$ = 336/465 nm).

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 m*M* 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 × 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+}.

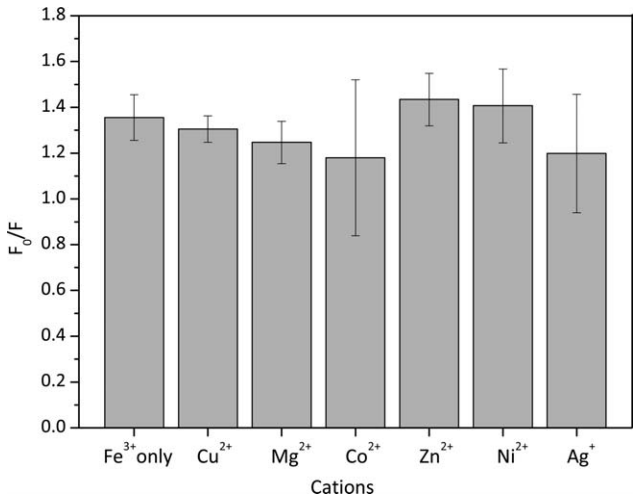

Figure 8. Quenching efficiency of fibers after being immersed into aqueous solution of Fe^{3+} (1.0 m*M*) only, and aqueous solution containing both Fe^{3+} (1.0 m*M*) and Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Ag^{+} (1.0 m*M*) ($\lambda_{Ex}/\lambda_{Em}$ = 336/465 nm).

ACKNOWLEDGMENTS

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Enhancing performance of optical sensor through the introduction of polystyrene and porous structures

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ABSTRACT: Simple and promising approaches for developing high-performance Fe^{3+} sensors were proposed. Polyvinyl chloride (PVC) membrane containing pyrene as a fluorescent indicator was prepared via solvent-cast method. Upon immersion into 1.0 m*M* Fe^{3+} solution, the fluorescence emission of the membrane decreased with the ratio of fluorescence intensities before and after (F_0/F) immersion of 1.25. The sensitivity enhancement was achieved through the introduction of polystyrene (PS) onto PVC and the introduction of porous structures. Polyvinyl chloride-*graft*-polystyrene copolymers (PVC-*g*-PS) were synthesized via Atom Transfer Radical Polymerization using PVC as macroinitiator. The grafting percentages of PS on PVC calculated from Nuclear Magnetic Resonance Spectroscopy were 17 and 41. The membrane prepared from low molecular weight copolymer showed higher sensing ability than that from PVC with the F_0/F value of 1.39. The increase in PS chain length did not significantly affect the fluorescence quenching. A Stern–Volmer quenching relationship was found with K_{sv} of 3.96×10^2 M^{-1}. The effect of porous structures on fluorescence quenching was studied by introducing Triton X-100 as a porogen to PVC/pyrene solution. Attenuated total reflection Fourier transform infrared spectroscopy and Scanning Electron Microscopy analyses confirmed a complete removal of Triton X-100 after 3 days of immersion in water. The porous membrane demonstrated an enhanced sensing performance with the F_0/F value of 1.46. PVC-*g*-PS/pyrene membrane exhibited highly sensitive and selective responses toward Fe^{3+} over Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Ag^{+}. In addition, a good reversibility after five cycles of quenching and regeneration was obtained. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41759.

KEYWORDS: grafting; optical properties; polyvinyl chloride; porous materials; sensors and actuators

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INTRODUCTION

Optical sensors have received considerable interests, and have been used for detections of various analytes including metal ions,[1–3] nitrite,[4] glucose,[5] methane,[6] and nitroaromatic compounds.[7,8] Suitable fluorescent indicators are used as recognition elements, and absorption and/or emission responses of these molecules resulting from interaction with target analytes are evaluated.

Compared with the detection in solution phase, solid-phase optical sensors offer an enhancement in stability, reversibility, and portability. In most solid-phase sensing designs, a sensing element is embedded in a polymer matrix such as polyvinyl alcohol, polyvinyl chloride (PVC), polyimides, polysilane, and cellulose acetate.[4,9–12] Monitoring iron traces in food and water samples is of great interest as high levels of ferric ion may induce various biological disorders and become toxic for organisms. Oter *et al.* immobilized a fluorescent benzofuran derivative in plasticized PVC matrix.[13] The immobilized dye demonstrated selective and reversible responses for Fe^{3+}. A spirolactam–rhodamine derivative was also utilized as recognition element for Fe^{3+} with good sensitivity and selectivity.[9] Among reported fluorescent indicators, pyrene has recently attracted considerable attention due to its large Stokes shift, strong absorbance, high quantum yield, excellent photostability, and relatively nontoxicity. Electrospun fibers from pyrene-functionalized poly(acrylic acid) were shown to effectively detect Fe^{3+}, Hg^{2+}, and 2,4-dinitrotoluene (DNT).[14] Wang *et al.* reported a high sensing performance of pyrene-doped electrospun polystyrene (PS) fibers toward nitroaromatics. The high

performance could possibly be attributed to the π–π stacking between pyrene and phenyl groups of PS, allowing efficient electron migration along the polymer chain.[15]

It is known that surface area plays an important role in sensing system that detects analytes by interacting with molecule on the surface. Numerous efforts have been carried out to increase the surface area of the surface in sensors; however, those involve complicated processes.[16,17] Recently, Yang *et al.* reported simple methods to generate porous structures into nanofibers by introducing a porogen and deacetylation treatment.[18] The sensitivity of the porous fibers of tetrakis(4-methoxylphenyl)porphyrin and PS toward DNT solution was enhanced drastically. In addition, porous cellulose acetate doped with 9-chloromethylanthracene nanofibers exhibited high response toward methyl violet.[12] The improvement in fluorescence quenching sensitivity could be attributed to the increased surface area, which provided easy accessibility of quenchers to diffuse into nanofibers.

In this work, fluorescence quenching-based sensing membranes for Fe^{3+} detection were prepared from solution of PVC and pyrene via solvent-cast method. Two approaches were carried out in order to improve the performance of the sensor. The first approach was to introduce PS onto PVC. Polyvinyl chloride-*graft*-polystyrene (PVC-*g*-PS) was synthesized via atom transfer radical polymerization (ATRP) using PVC as macroinitiator. Sensing performance of pyrene-doped membranes prepared from PVC graft copolymer was compared with that from PVC homopolymer. The effect of PS chain length on fluorescence quenching was also studied. The second approach was to introduce porous structures to PVC and PVC-*g*-PS membranes using Triton X-100 as a porogen. The effect of membrane porosity on quenching was investigated. The sensitivity and selectivity toward Fe^{3+} and other metal ions, and the reusability of the prepared membranes were discussed.

EXPERIMENTAL

Materials

PVC (M_W 43,000, M_n 22,000), styrene (>99%), pyrene (>98%), aluminum oxide (basic), copper (I) bromide (CuBr, >98%), iron (III) nitrate nonahydrate, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, >99%), and 1-methyl-2-pyrrolidinone (NMP, 99%) were purchased from Sigma-Aldrich (The United States). Triton X-100 was obtained from Merck (The United States). Magnesium (II) sulfate heptahydrate, zinc chloride, and silver nitrate were supplied by Carlo Erba Reagents (Thailand). Nickel (II) sulfate hexahydrate and cobalt (II) nitrate hexahydrate were purchased from Guangdong Guanghua Chemical Factory Co. Ltd (China). Copper (II) nitrate hemipentahydrate and ethylenediaminetetraacetic acid disodium salt (Na_2EDTA, 99%) were obtained from Ajax Finechem (Thailand). All chemicals were used as received.

Synthesis of PVC-*g*-PS

PVC-*g*-PS was synthesized via ATRP and the procedures were as follows: PVC (5.0007 g) was dissolved in NMP (40.0 mL) in a round bottom flask at room temperature for 5 h. Styrene was purified by passing through a short column of basic alumina. Styrene (10.0135 g), PMDETA (290 μL, 1.39 mmol), and CuBr (0.2004 g, 1.39 mmol) were then added to PVC solution. The solution was flushed with N_2 for 15 min, and then stirred at 90 °C for 7 h. After polymerization, the residual copper catalyst was removed by passing the reaction mixture down a short column filled with basic alumina. The polymer solution was concentrated and precipitated in methanol. In the synthesis of PVC-*g*-PS with higher molecular weight, the amounts of PMDETA and CuBr were doubled.

Membrane Preparation

A 5 wt % polymer (PVC or PVC-*g*-PS) solution was prepared by dissolving polymer and pyrene (20% by weight of polymer) in tetrahydrofuran (THF). The solution was stirred for 24 h prior to casting on a petri dish. The membrane was dried at room temperature, and later peeled off. In a preparation of porous membrane, Triton X-100 was added to polymer/pyrene solution prior to stirring for 24 h. The weight ratio of polymer and Triton X-100 was 1: 1. The solvent-cast membrane was dried at room temperature, and later peeled off. Due to the water solubility of Triton X-100, it was consequently washed away from the membrane by immersing in deionized (DI) water with a shaking speed of 120 rpm.

Characterization

^{1}H-nuclear magnetic resonance (^{1}H-NMR) (400 MHz) spectra were obtained on a Varian Mercury-400 NMR Spectrometer with the samples dissolved in chloroform-d containing tetramethylsilane (TMS). Molecular weight was measured by Gel Permeation Chromatography (GPC) in THF at 40 °C with a flow rate of 1.0 mL/min on a system equipped with Styragel HR5E column, and refractive index detector (waters 2414). PS standards were used for molecular weight calibration. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were measured on a Bruker FTIR spectrometer (Tensor 27) with Opus 7.0 software. Emission spectra were recorded using an RF-5301PC spectrofluorophotometer (Shimadzu) with excitation/emission slit widths of 3/5 nm (low sensitivity) for PVC/pyrene and PVC/pyrene/Triton X-100 membranes, 1.5/3 nm (high sensitivity) for low molecular weight PVC-*g*-PS/pyrene membrane, 3/1.5 nm (high sensitivity) for high molecular weight PVC-*g*-PS/pyrene membrane, and 5/5 nm (low sensitivity) for PVC-*g*-PS/pyrene/Triton X-100 membranes. Membranes were gold-coated prior to imaging by a Scanning Electron Microscope (SEM, SEC Co., Ltd., SNE-4500M). The average pore sizes were determined from 200 pore diameters in each micrograph using WCIF ImageJ program.

Sensitivity Study

Response performance of membranes toward Fe^{3+} ions was carried out as follows. The membranes 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 emissions at 470, 483, and 485 nm (F_0) were recorded for PVC, low molecular weight PVC-*g*-PS, and high molecular weight PVC-*g*-PS, respectively. The membranes were then immersed into 1.0 m*M* aqueous ferric nitrate solution for 30 min. After thorough washing with water, the membranes were dried prior to fluorescence emission measurements (F). The mean of three fluorescence emission measurements was used for each sample, and the

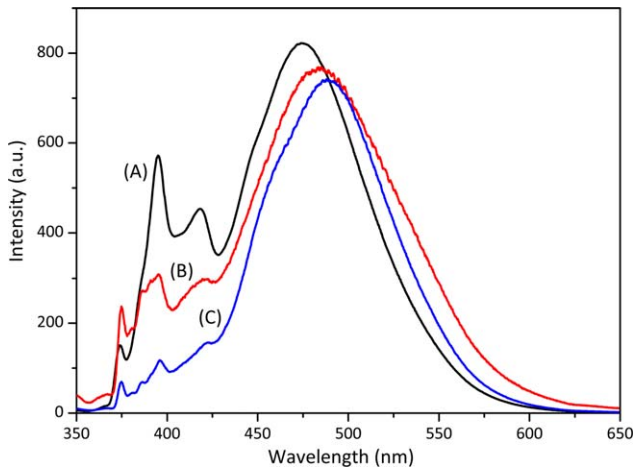


Figure 1. Emission spectra of PVC/pyrene membrane (**A**), low molecular weight PVC-*g*-PS/pyrene membrane (**B**), and high molecular weight PVC-*g*-PS/pyrene membrane (**C**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported F_0/F value was the mean of two replicates. In a study of the effect of Fe^{3+} concentration on fluorescence quenching, high molecular weight PVC-*g*-PS/pyrene membrane was immersed into ferric nitrate solutions of different concentrations ranging from 0 to 1.0 m*M*.

Selectivity and Interference Studies

To investigate the selectivity of the membrane prepared from low molecular weight PVC-*g*-PS toward metal ions, 1.0 m*M* 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 m*M*) and other selected metal ion (1.0 m*M*) were used in interference study.

Reusability Study

The reusability study was conducted as follows.[9] After immersing PVC-*g*-PS membrane into 1.0 m*M* Fe^{3+} solution for 30 min, the membrane was washed with water, and later immersed into the saturated Na_2EDTA solution for 30 min. The membrane was washed with water, and dried prior to fluorescence emission measurements.

RESULTS AND DISCUSSION

PVC/Pyrene Membrane

Membrane Preparation and Emission Spectrum. Free standing membrane with a thickness of 0.21 mm was obtained from PVC/pyrene solution. Emission spectrum of pyrene-doped PVC membrane is shown in Figure 1(A). The two major bands between 370 and 420 nm and centered at 470 nm could be ascribed to the emission from excited pyrene monomer, and pyrene excimer, respectively.[19–21]

Fluorescence quenching can be described by Stern–Volmer equation

$$F_0/F = 1 + K_{sv}[Q] \quad (1)$$

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 470 nm of pyrene-doped PVC membrane before and after immersion in 1.0 m*M* Fe^{3+} solution (F_0/F) for 30 min was 1.25. The fluorescence quenching could be due to interactions of electron-rich dye, pyrene, and electron-deficient quencher, Fe^{3+}, via a photo-induced electron transfer mechanism (PET) and/or electronic energy transfer.[22]

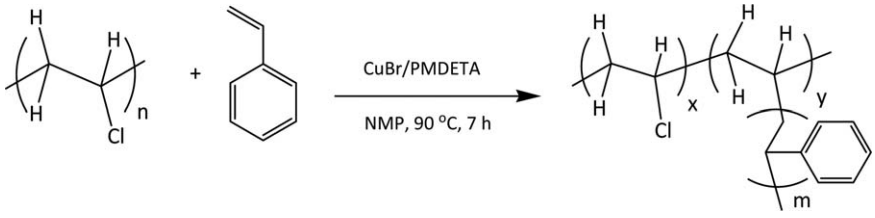
Effect of Immersion Period in Fe^{3+} Solution on Quenching. Another piece of the prepared membrane was immersed into 1.0 m*M* Fe^{3+} solution for 90 min. The average F_0/F value was found to be 1.21. Since there was no significant difference in fluorescence quenching between using the immersion periods of 30 and 90 min, the immersion period of 30 min was selected for sensing performance studies.

PVC-*g*-PS/Pyrene Membranes: Effects of Polymeric Matrix and PS Chain Length on Quenching

PVC-*g*-PS Synthesis. PVC-*g*-PS was synthesized via ATRP using PVC as macroinitiator and CuBr/PMDETA catalyst system. PVC-*g*-PS copolymers with two different PS chain lengths were obtained by varying the amounts of CuBr and PMDETA. The synthetic scheme was shown in Scheme 1. Successful synthesis was confirmed by ^{1}H-NMR spectra in Figure 2. The peaks around 4.5 ppm corresponded to CHCl of PVC. Upon grafting PS onto PVC, two additional peaks around 6.5 and 7.1 ppm were shown. The grafting percentage was calculated from the integrals of peaks from PS at 6.5 and 7.1 ppm, and that from PVC at 4.5 ppm. Grafting percentages of PS onto PVC of the two polymers were 17 and 41.

The number-average molecular weights and polydispersity indices (PDI) obtained from GPC of the two PVC-*g*-PS copolymers were 32,100 (PDI 2.38), and 69,800 (PDI 2.22). A unimodal GPC peak with a small increase in PDI compared with that of PVC homopolymer suggested that there was no homopolymer contamination or coupling reactions.

Sensing Performance of PVC-*g*-PS/Pyrene Membranes. The emission spectrum of low molecular weight PVC-*g*-PS/pyrene membrane in Figure 1(B) showed a red shift of the excimer



Scheme 1. Synthesis of PVC-*g*-PS via ATRP.

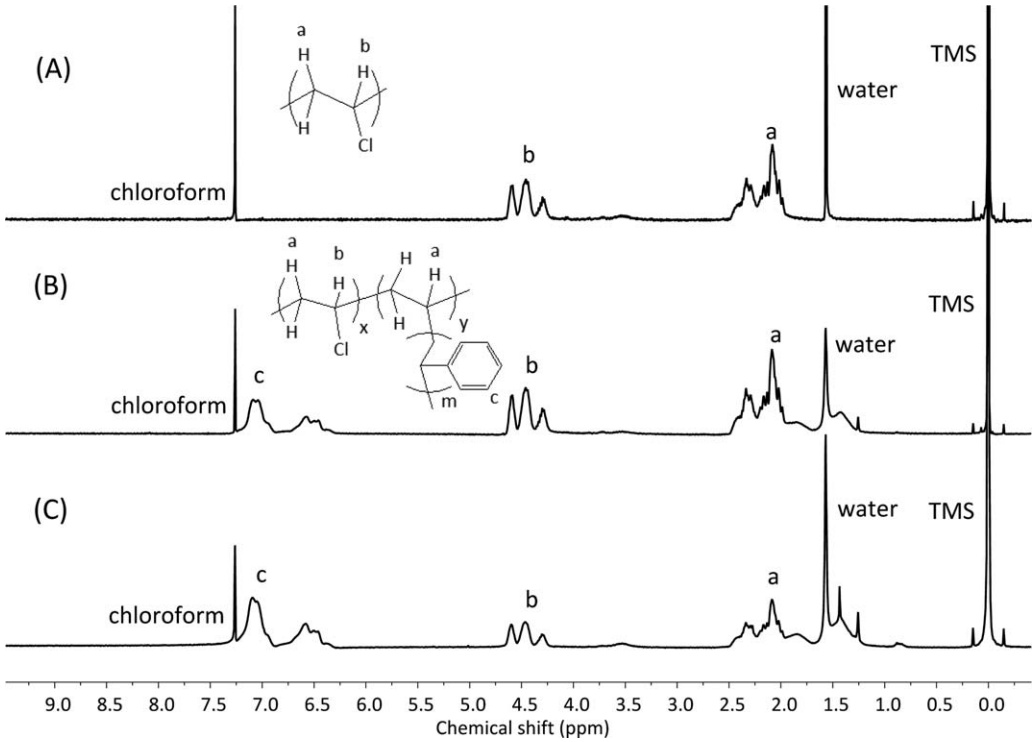


Figure 2. NMR spectra of PVC (**A**), low molecular weight PVC-*g*-PS (**B**), and high molecular weight PVC-*g*-PS (**C**).

emission relative to that of PVC/pyrene membrane by 13 nm to 483 nm, indicating a formation of pyrene aggregation.[23] It was also found that as PS chain length was increased, the excimer emission was further shifted to a longer wavelength.

Sensing performances toward 1.0 m*M* Fe^{3+} solution of membranes prepared from the two graft copolymers were compared with that from PVC. PVC-*g*-PS membranes showed higher sensing abilities with F_0/F values of 1.39 and 1.38 for low molecular weight and high molecular weight, respectively. The pronounced sensitivity could possibly be due to the co-facial π–π stacking between the phenyl side chains of PS and pyrene ("molecular wire" amplification).[15,24] The π conjugated system increases the possibility of interaction between pyrene and Fe^{3+}, leading to high fluorescence quenching. The enhancement in sensing performance through enlarging the effective conjugation degree of π system has also been observed in other pyrene-based

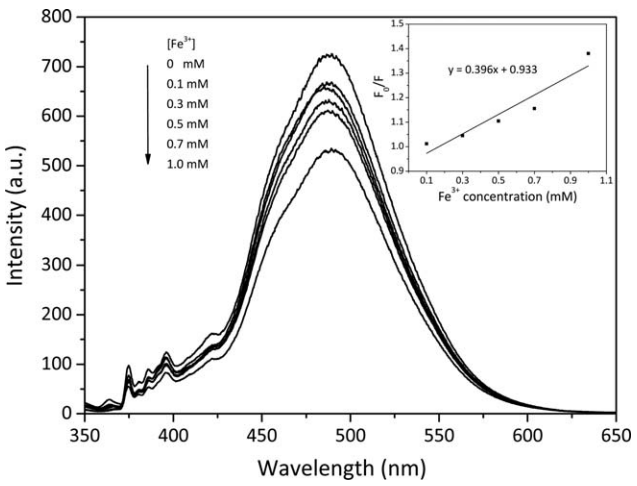


Figure 3. Fluorescence spectra change of high molecular weight PVC-*g*-PS/pyrene membrane as a function of Fe^{3+} concentration; [Fe^{3+}] = 0–1.0 m*M* (from top to bottom) and corresponding Stern–Volmer plot (inset). ($\lambda_{Ex}/\lambda_{Em}$ = 336/485 nm).

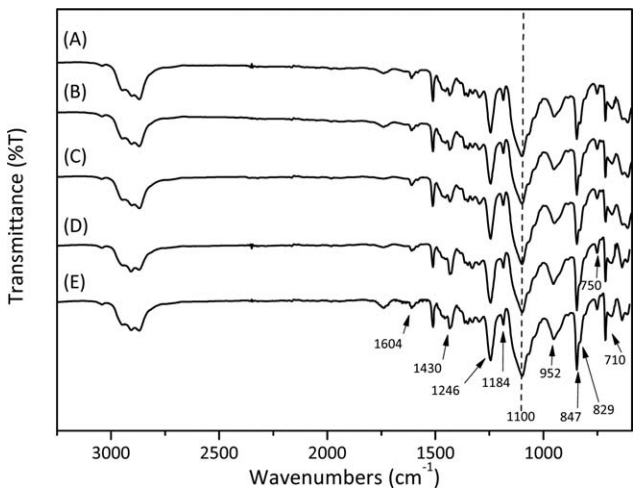


Figure 4. ATR-FTIR spectra of PVC/pyrene membrane containing Triton X-100 before (**A**) and after immersion in water for 1 day (**B**), 2 days (**C**), 3 days (**D**), and 4 days (**E**).

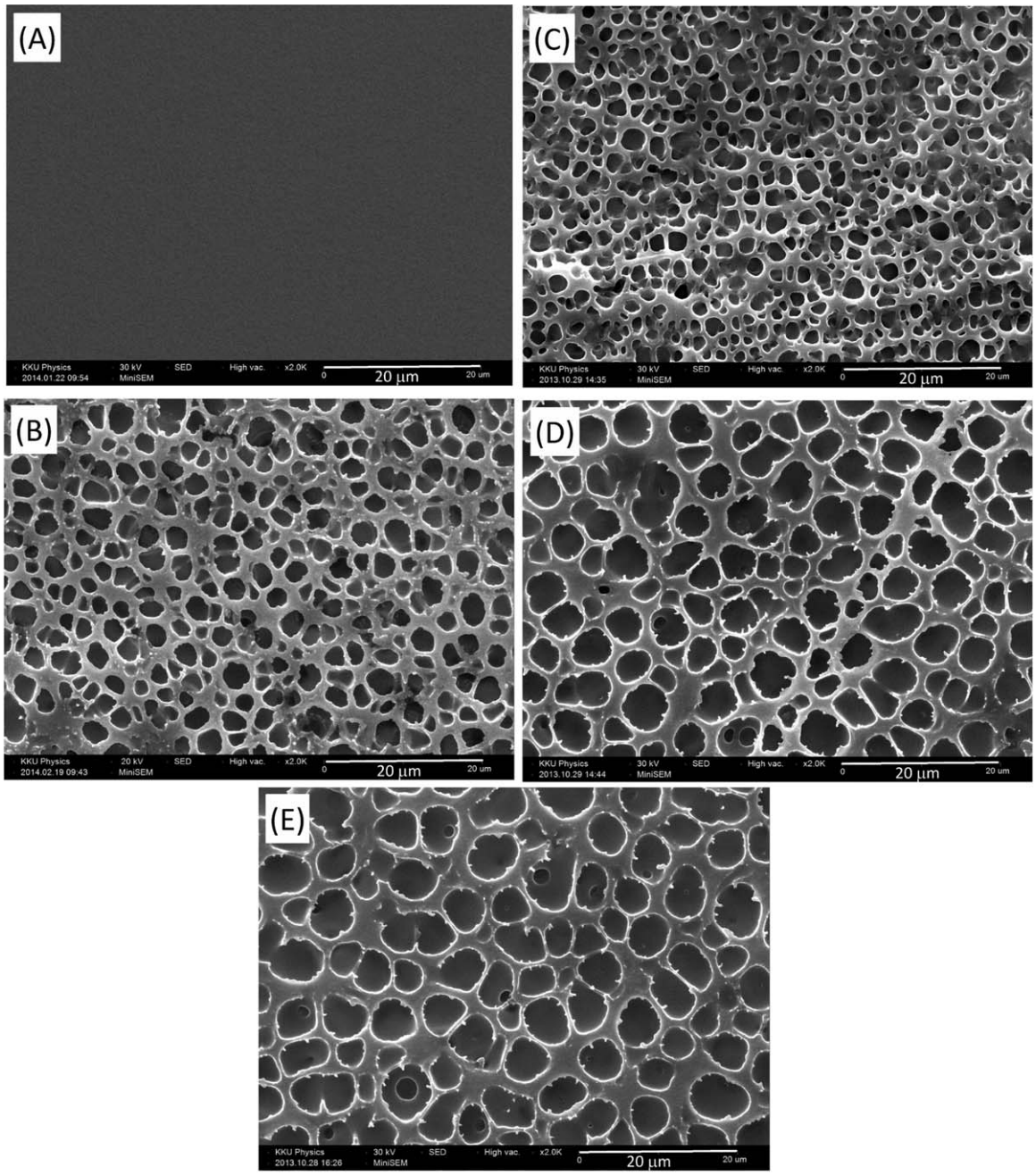


Figure 5. SEM images (2k magnification) of PVC/pyrene/Triton X-100 membranes before (**A**) and after immersion in water for 1 day (**B**), 2 days (**C**), 3 days (**D**), and 4 days (**E**). The average pore sizes of (B), (C), (D), and (E) were 2.25 ± 0.70, 2.51 ± 0.63, 4.13 ± 1.31, and 4.92 ± 1.60, respectively. Scale bar is 20 μm.

fluorescent sensors.[25–27] No drastic change in quenching ability was observed when PS chain was extended. Despite a much lower surface area, which could be 1–2 orders of magnitudes lower,[28] these continuous pyrene-doped PVC-*g*-PS membranes showed comparable Fe^{3+} response performance to our micron-size fibers from poly(methyl methacrylate), poly(vinyl chloride-*co*-vinyl acetate-*co*-vinyl alcohol) and pyrene.[29]

The effect of Fe^{3+} concentration on fluorescence intensity of high molecular weight PVC-*g*-PS/pyrene membrane was shown in Figure 3. The intensity was found to gradually decrease with increasing Fe^{3+} concentration. A linear plot between Fe^{3+} concentration and F_0/F provided a K_{sv} value of $3.96 \times 10^2\ M^{-1}$.

PVC/Pyrene/Triton X-100 Membranes: Effect of Porosity on Quenching

Preparation of Porous PVC Membrane. Another approach to improve the sensing performance of PVC/pyrene membrane was conducted through the introduction of porous structures using Triton X-100 as a water-soluble porogen. ATR-FTIR spectra of PVC/pyrene/Triton X-100 membranes before and after immersion in water were shown in Figure 4. Characteristic bands of

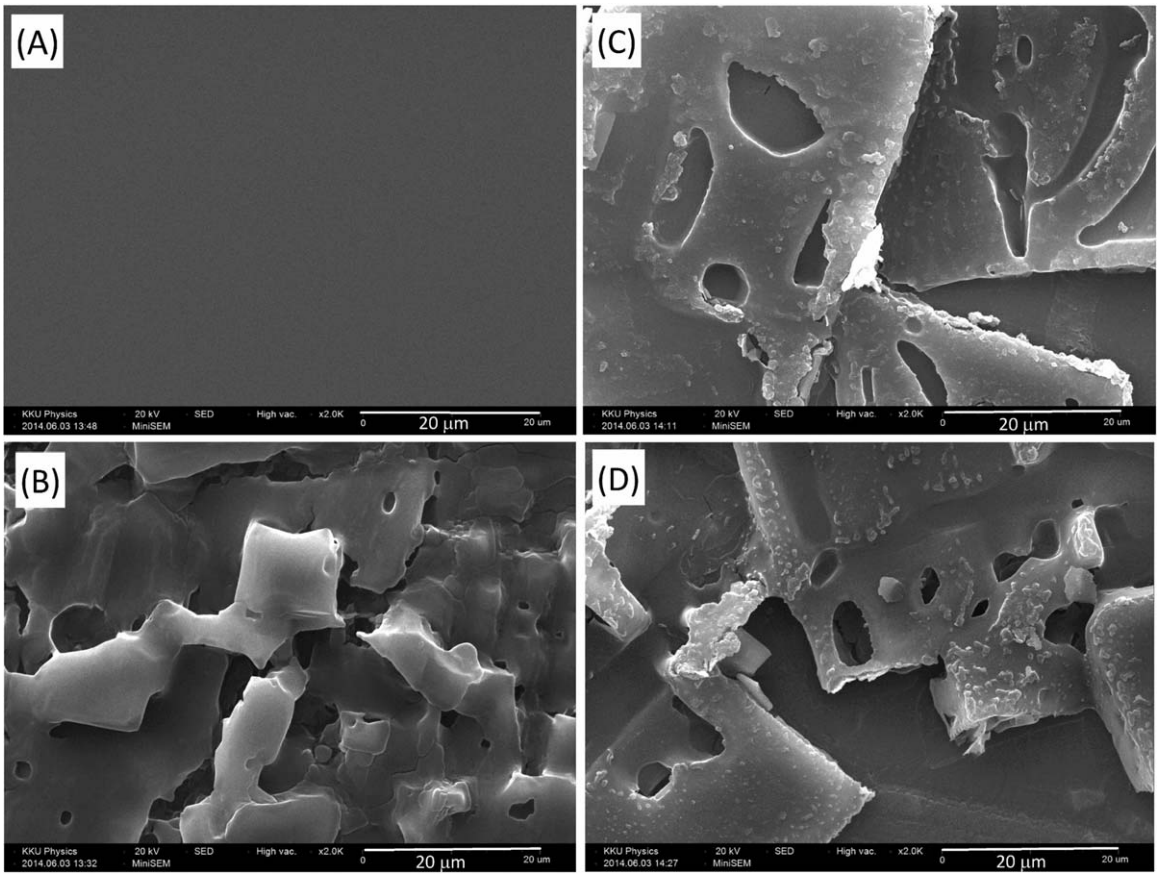


Figure 6. SEM images (2k magnification) of PVC-*g*-PS/pyrene/Triton X-100 membranes before (**A**) and after immersion in water for 3 days (**B**), 4 days (**C**), and 5 days (**D**). Scale bar is 20 μm.

PVC at 1246, 952, and 847 cm^{-1} were assigned to C—H rocking, C—H wagging, and C—Cl stretching, respectively.[30] The band corresponding to C—C stretching was also present at 1096 cm^{-1}. The bands at 1604, 1430, and 829 cm^{-1} of pyrene were assigned to C=C stretchings and bands at 1184, 750, and 710 cm^{-1} were assigned to three adjacent C—H stretchings.[31] The band relating to C—O stretching of Triton X-100 was shown at 1100 cm^{-1}, overlapping with the C—C stretching band of PVC. A decrease of band intensity at 1100 cm^{-1} suggested a complete removal of Triton X-100 after 3 days of immersion in water.

SEM images of pyrene-doped PVC/Triton X-100 membranes before and after immersion in water for 1, 2, 3, and 4 days were shown in Figure 5. Similar pore sizes were observed after 3 and

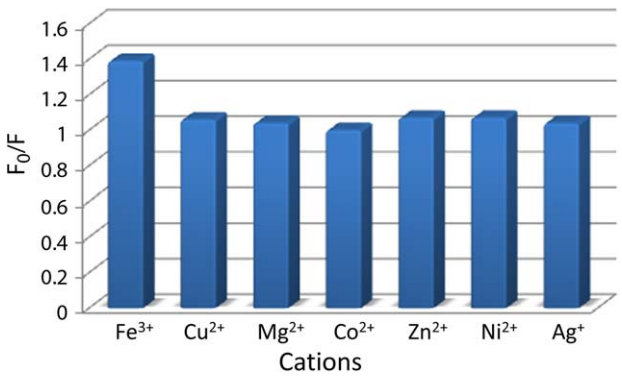


Figure 7. Responses of PVC-*g*-PS membranes to 1.0 m*M* solutions of various metal cations. ($\lambda_{Ex}/\lambda_{Em}$ = 336/483 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

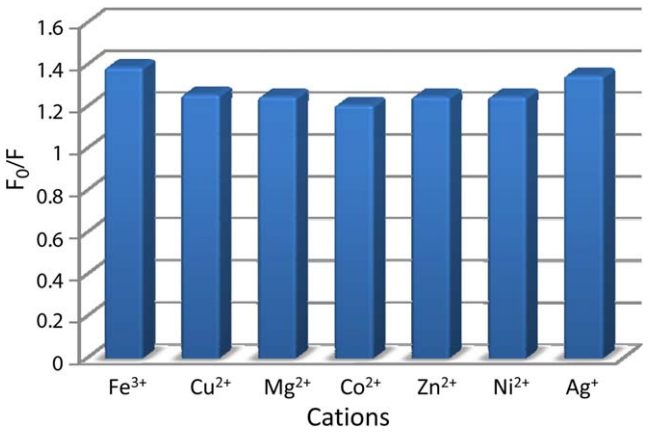


Figure 8. Quenching efficiencies of PVC-*g*-PS membranes after being immersed into solution of Fe^{3+} (1.0 m*M*) only, and solutions containing both Fe^{3+} (1.0 m*M*) and other metal ion (1.0 m*M*). ($\lambda_{Ex}/\lambda_{Em}$ = 336/483 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

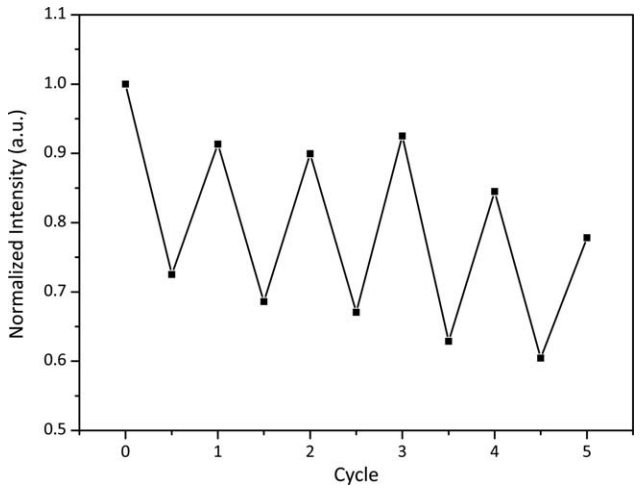


Figure 9. Fluorescence intensities of PVC-*g*-PS membrane after alternate treatment by solutions of Fe^{3+} and Na_2EDTA. ($\lambda_{Ex}/\lambda_{Em}$ = 336/483 nm).

4 days of immersion, suggesting that Triton X-100 was completely removed after 3 days. Since FTIR results had good agreement with SEM analysis, immersion in water for 3 days was chosen for further investigations.

Sensing Performance of Porous PVC/Pyrene Membrane. Prior to Fe^{3+} sensing study, fluorescence emissions of PVC/pyrene/Triton X-100 membranes before and after immersion in water for 3 days were compared. Similar fluorescence intensities suggested that there was no pyrene leakage during Triton X-100 removal. Sensing performance of PVC membrane with porous structures was then evaluated. The higher F_0/F value of 1.46 of the porous membrane is likely attributed to the increased surface area which provides faster diffusion of the quencher to the sensing elements.

PVC-*g*-PS/Pyrene/Triton X-100 Membranes: Effect of Both PS and Porosity on Quenching

Preparation and Sensing Performance of Porous PVC-*g*-PS/Pyrene Membranes. The effect of both PS incorporation and porous structures on fluorescence quenching was further explored. Porous PVC-*g*-PS membrane was prepared as described for porous PVC membrane. Figure 6 displayed SEM images of the membranes before and after immersion in water for 3, 4, and 5 days. Rough surfaces with non-uniform pores were observed after being immersed in water. FTIR results (data not shown) suggested a complete removal of Triton X-100 after 3 days of immersion. The fluorescence quenching ability of this porous membrane was investigated. A relatively low sensing performance with the F_0/F value of 1.21 could possibly be due to a reduction in number of small pores, that is, a decrease in surface area, and a decrease in long-range exciton migration between PS and pyrene created from non-uniform porous structures.

Selectivity and Interference Studies of PVC-*g*-PS/Pyrene Membranes

Although a large number of porous structures in PVC/pyrene membrane offered such a high sensitivity, they also made the membrane more brittle. Therefore, the PVC-*g*-PS/pyrene membrane was chosen for selectivity and interference studies.

The selectivity of the sensing membrane prepared from low molecular weight PVC-*g*-PS was evaluated by immersing the membrane into 1.0 m*M* aqueous solutions of Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Ag^{+}. Figure 7 revealed that the membrane was 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 1.39, 1.06, 1.04, 1.00, 1.07, 1.07, and 1.04, respectively. The interference effect of other metal ions on quenching ability of Fe^{3+} was also studied. Similar F_0/F values in Figure 8 indicated that the binding of Fe^{3+} to pyrene was not interrupted by the presence of other selected ions.

Reusability Study

The low molecular weight PVC-*g*-PS membrane was alternately exposed to 1.0 m*M* Fe^{3+} solution and saturated Na_2EDTA solution. The corresponding fluorescence emission was measured. As shown in Figure 9, the membrane showed good reversibility with less than 22% signal loss after five cycles of quenching and regeneration. Since Fe^{3+} forms a stronger complex with Na_2EDTA than with pyrene, the reversibility could be obtained.

CONCLUSIONS

This work provides simple and efficient approaches to fabricate fluorescence quenching-based optical sensor for Fe^{3+} detection. Self-standing pyrene-doped PVC membrane was prepared via solvent-cast method. The sensitivity was enhanced through the introduction of PS onto PVC via ATRP and the introduction of porous structures using Triton X-100 as a porogen. PS chain length did not significantly affect the quenching ability of the membrane. The ratios of fluorescence intensities of low molecular weight PVC-*g*-PS membrane and porous PVC membrane before and after (F_0/F) immersion in Fe^{3+} solution were 1.39 and 1.46, respectively. Introductions of both PS and porous structures did not result in an improvement in sensing performance in this study. PVC-*g*-PS membrane exhibited highly sensitive and selective responses toward Fe^{3+} over other selected metal ions with good reusability.

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Ferric Ion Sensor Based on Polyvinyl Chloride and Polyvinyl Chloride-*graft*-Polystyrene Membranes

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Pyrene-doped poly(vinyl chloride) (PVC) membrane for ferric ion (Fe^{3+}) detection was prepared from solution of PVC and 20% pyrene in tetrahydrofuran (THF) via solvent-cast method. The effect of immersion period (30, 60 and 90 minutes) in 1.0 mM Fe^{3+} solution of the membrane on fluorescence quenching was studied, and no significant change in fluorescence quenching was observed. The ratio of fluorescence intensities of the membrane before and after (F_0/F) immersion in Fe^{3+} solution was approximately 1.20. To explore the effect of polymeric matrix on quenching, polyvinyl chloride-*graft*-polystyrene (PVC-*g*-PS) was synthesized via Atom Transfer Radical Polymerization (ATRP) using PVC as macroinitiator. Successful synthesis was confirmed by Nuclear Magnetic Resonance Spectroscopy (NMR), and grafting percentage was calculated to be 23%. The increase in molecular weight relative to PVC homopolymer characterized by Gel Permeation Chromatography (GPC) also confirmed the grafting of PS on PVC. A unimodal GPC peak with relatively narrow molecular weight distribution of the copolymer suggested that there was no homopolymer contamination or coupling reactions. The membrane prepared from PVC graft copolymer showed higher sensing ability with F_0/F value of 1.40.

Keywords Poly(vinyl chloride); Graft copolymers; Sensors

Effect of Polystyrene Incorporation on Ferric Ion Detection

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Abstract

Optical sensor membranes for ferric ion (Fe^{3+}) detection were prepared from solution of polyvinyl chloride (PVC) or polyvinyl chloride-*graft*-polystyrene (PVC-*g*-PS) and pyrene as a fluorophore. The fluorescence intensity of PVC/pyrene membrane decreased upon the introduction of Fe^{3+}. The ratio of fluorescence intensities before and after (F_0/F) immersion in 1.0 mM Fe^{3+} solution for 30 minutes was 1.25. To study the effects of polymeric matrix and PS chain length on fluorescence quenching, PVC-*g*-PS copolymers with two different molecular weights were synthesized via Atom Transfer Radical Polymerization (ATRP) using PVC as macroinitiator. The grafting percentages of PS on PVC calculated from Nuclear Magnetic Resonance Spectroscopy (NMR) were 17 and 41, and the number average molecular weights (M_n) obtained from Gel Permeation Chromatography (GPC) were 32,100 g/mol and 69,700 g/mol, respectively. It was found that membranes prepared from PVC-*g*-PS showed higher quenching ability with the F_0/F values of 1.39 for the low M_n copolymer and 1.37 for the high M_n copolymer. In addition, the low M_n PVC-*g*-PS membrane exhibited a highly selective response toward Fe^{3+} over Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Ag^{+}.

Keywords: Atom Transfer Radical Polymerization (ATRP), Fluorescence, Graft copolymer, Sensor