

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

Chonnakarn Panawong,<sup>1,2</sup> Thidarat Pandhumas,<sup>3</sup> Sujittra Youngme,<sup>3</sup> Surangkhan Martwiset<sup>2,3</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

<sup>2</sup>Nanotec-KKU Center of Excellence on Advanced Nanomaterials for Energy Production and Storage, Khon Kaen University, Khon Kaen 40002, Thailand

<sup>3</sup>Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

Correspondence to: S. Martwiset (E-mail: surama@kku.ac.th)

**ABSTRACT:** Simple and promising approaches for developing high-performance  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  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  $3.96 \times 10^2 \text{ M}^{-1}$ . 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  $\text{Fe}^{3+}$  over  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Ag}^+$ . 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,<sup>1–3</sup> nitrite,<sup>4</sup> glucose,<sup>5</sup> methane,<sup>6</sup> and nitroaromatic compounds.<sup>7,8</sup> 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.<sup>4,9–12</sup> 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.<sup>13</sup> The immobilized dye demonstrated selective and reversible responses for  $\text{Fe}^{3+}$ . A spirolactam–rhodamine derivative was also utilized as recognition element for  $\text{Fe}^{3+}$  with good sensitivity and selectivity.<sup>9</sup> 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  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ , and 2,4-dinitrotoluene (DNT).<sup>14</sup> 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  $\pi$ - $\pi$  stacking between pyrene and phenyl groups of PS, allowing efficient electron migration along the polymer chain.<sup>15</sup>

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.<sup>16,17</sup> Recently, Yang *et al.* reported simple methods to generate porous structures into nanofibers by introducing a porogen and deacetylation treatment.<sup>18</sup> The sensitivity of the porous fibers of tetrakis(4-methoxyphenyl)porphyrin and PS toward DNT solution was enhanced drastically. In addition, porous cellulose acetate doped with 9-chloromethylantracene nanofibers exhibited high response toward methyl violet.<sup>12</sup> 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  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  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 ( $\text{Na}_2\text{EDTA}$ , 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  $\mu\text{L}$ , 1.39 mmol), and CuBr

(0.2004 g, 1.39 mmol) were then added to PVC solution. The solution was flushed with  $\text{N}_2$  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

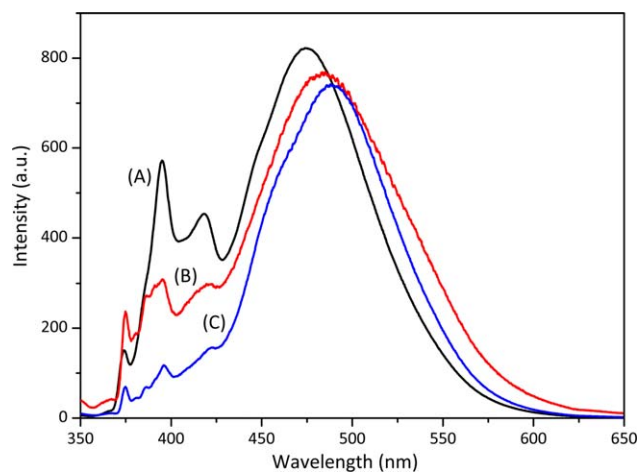
A 5 wt % polymer (PVC or PVC-g-PS) solution was prepared by dissolving polymer and pyrene (20% by weight of polymer) in tetrahydrofuran (THF). The solution was stirred for 24 h prior to casting on a petri dish. The membrane was dried at room temperature, and later peeled off. In a preparation of porous 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

$^1\text{H}$ -nuclear magnetic resonance ( $^1\text{H-NMR}$ ) (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  $\text{Fe}^{3+}$  ions was carried out as follows. The membranes were cut into 1 cm  $\times$  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 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](http://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 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.<sup>9</sup> After immersing PVC-g-PS membrane into 1.0 mM  $Fe^{3+}$  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.<sup>19–21</sup>

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 mM  $Fe^{3+}$  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.<sup>22</sup>

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

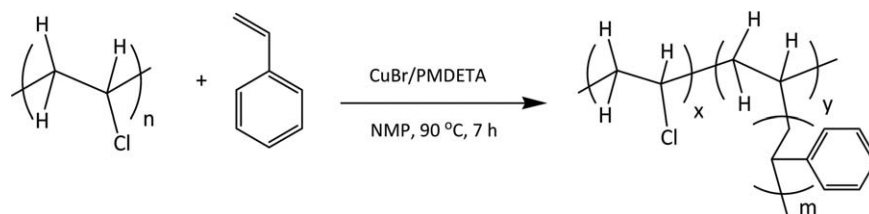
Another piece of the prepared membrane was immersed into 1.0 mM  $Fe^{3+}$  solution for 90 min. The average  $F_0/F$  value was found to be 1.21. Since there was no significant difference in fluorescence quenching between using the immersion periods of 30 and 90 min, the immersion period of 30 min was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

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

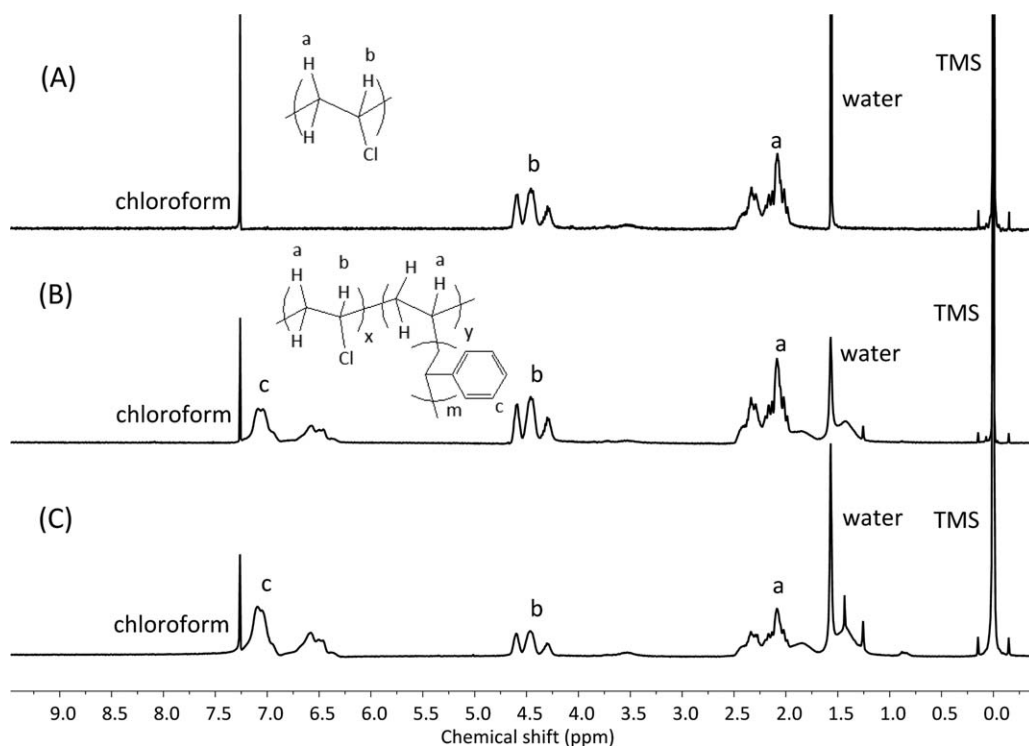
**PVC-g-PS Synthesis.** PVC-g-PS was synthesized via ATRP using PVC as macroinitiator and  $CuBr/PMDETA$  catalyst system. PVC-g-PS copolymers with two different PS chain lengths were obtained by varying the amounts of  $CuBr$  and  $PMDETA$ . The synthetic scheme was shown in Scheme 1. Successful synthesis was confirmed by  $^1H-NMR$  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.

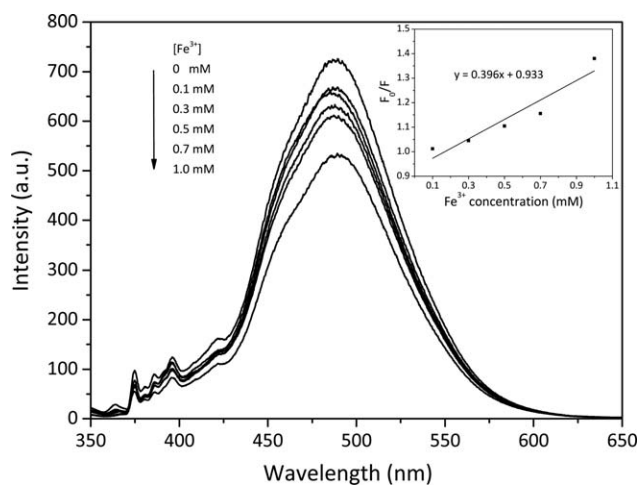


**Figure 2.** NMR spectra of PVC (A), low molecular weight PVC-g-PS (B), and high molecular weight PVC-g-PS (C).

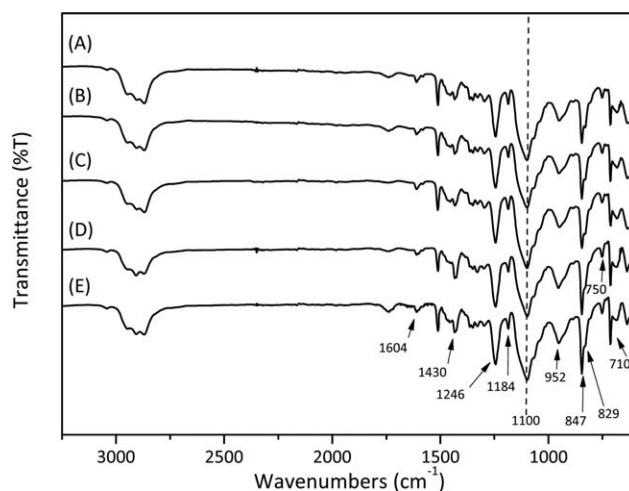
emission relative to that of PVC/pyrene membrane by 13 nm to 483 nm, indicating a formation of pyrene aggregation.<sup>23</sup> It was also found that as PS chain length was increased, the excimer emission was further shifted to a longer wavelength.

Sensing performances toward 1.0 mM Fe<sup>3+</sup> 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

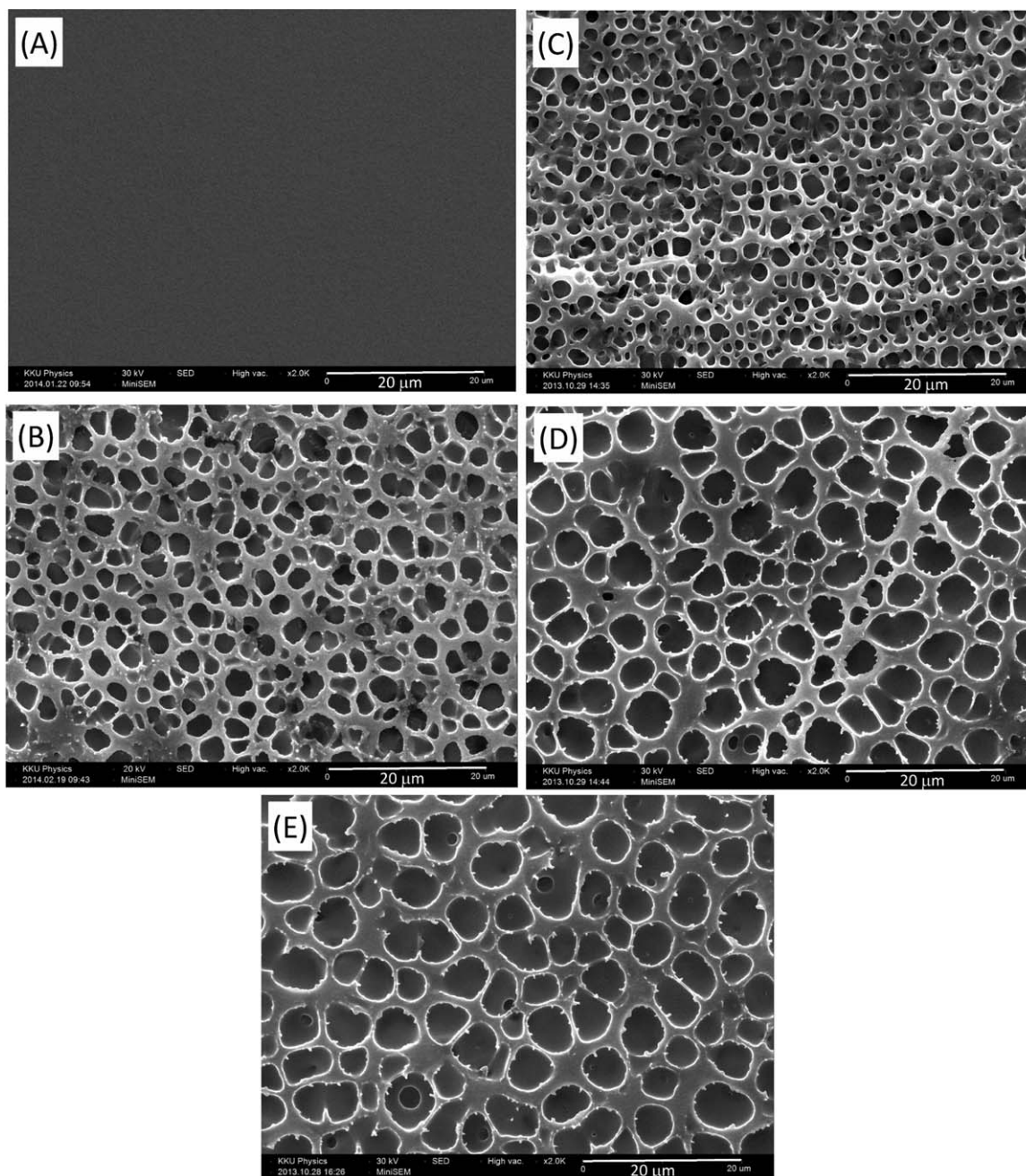
weight and high molecular weight, respectively. The pronounced sensitivity could possibly be due to the co-facial  $\pi$ - $\pi$  stacking between the phenyl side chains of PS and pyrene ("molecular wire" amplification).<sup>15,24</sup> The  $\pi$  conjugated system increases the possibility of interaction between pyrene and Fe<sup>3+</sup>, leading to high fluorescence quenching. The enhancement in sensing performance through enlarging the effective conjugation degree of  $\pi$  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<sup>3+</sup> concentration; [Fe<sup>3+</sup>] = 0–1.0 mM (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  $2.25 \pm 0.70$ ,  $2.51 \pm 0.63$ ,  $4.13 \pm 1.31$ , and  $4.92 \pm 1.60$ , respectively. Scale bar is 20  $\mu\text{m}$ .

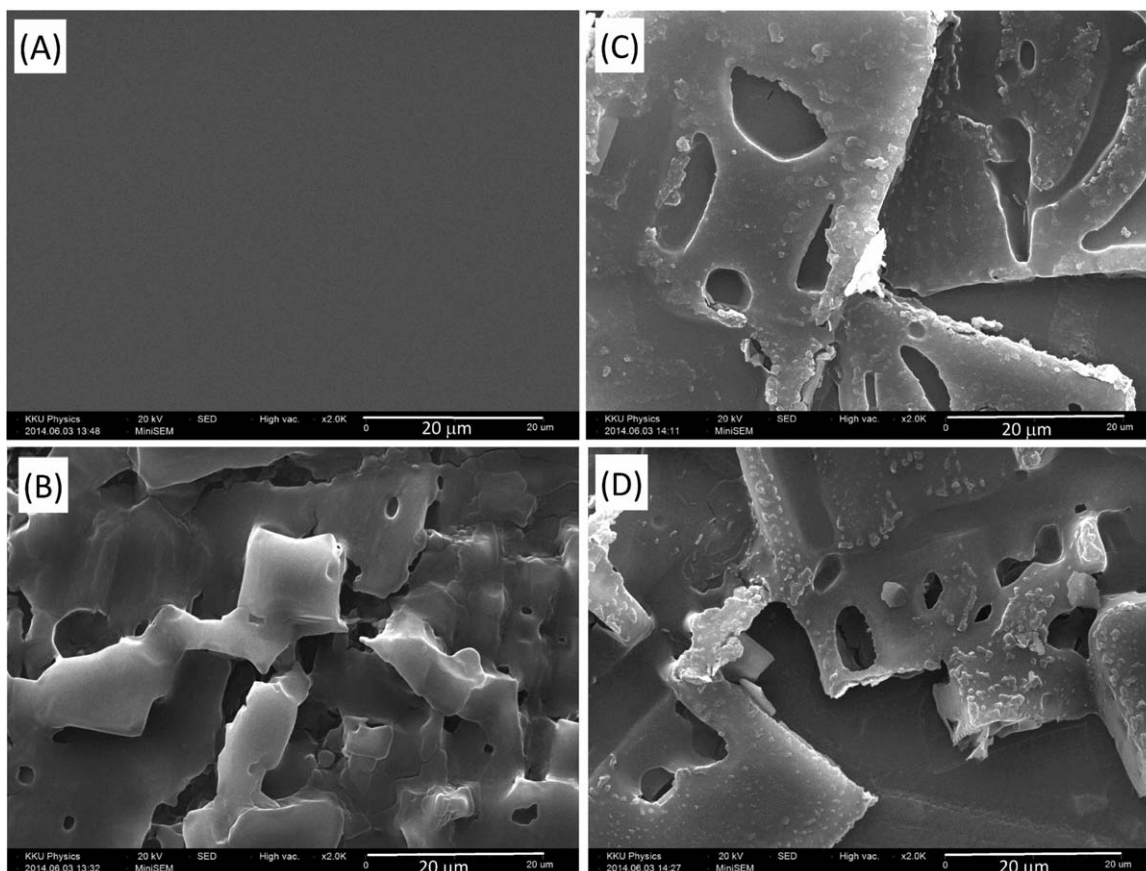
fluorescent sensors.<sup>25–27</sup> No drastic change in quenching ability was observed when PS chain was extended. Despite a much lower surface area, which could be 1–2 orders of magnitudes lower,<sup>28</sup> these continuous pyrene-doped PVC-g-PS membranes showed comparable  $\text{Fe}^{3+}$  response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

The effect of  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  concentration. A linear plot between  $\text{Fe}^{3+}$  concentration and  $F_0/F$  provided a  $K_{sp}$  value of  $3.96 \times 10^2 \text{ M}^{-1}$ .

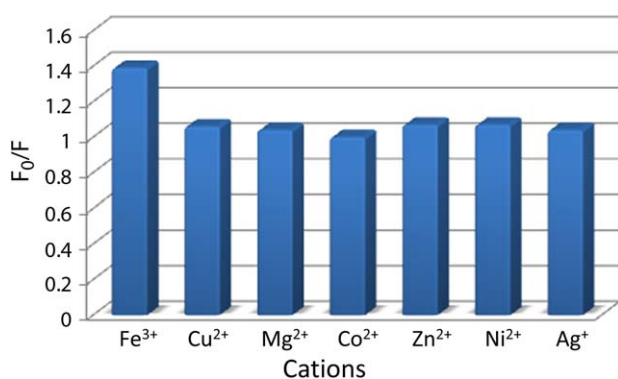
#### PVC/Pyrene/Triton X-100 Membranes: Effect of Porosity on Quenching

**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.

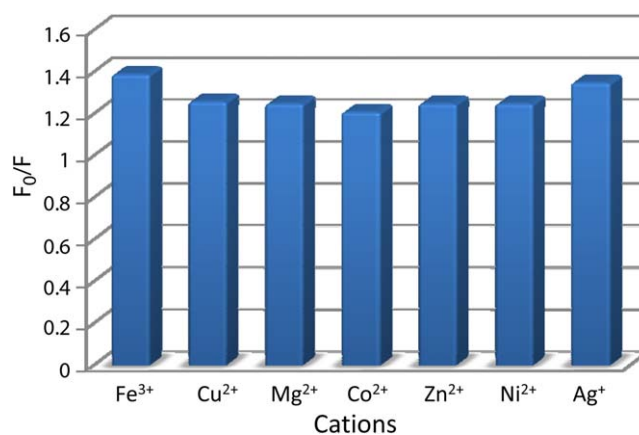
PVC at 1246, 952, and 847  $\text{cm}^{-1}$  were assigned to C—H rocking, C—H wagging, and C—Cl stretching, respectively.<sup>30</sup> The band corresponding to C—C stretching was also present at 1096  $\text{cm}^{-1}$ . The bands at 1604, 1430, and 829  $\text{cm}^{-1}$  of pyrene were assigned to C=C stretchings and bands at 1184, 750, and 710  $\text{cm}^{-1}$  were assigned to three adjacent C—H stretchings.<sup>31</sup> The band relating to C—O stretching of Triton X-100 was shown at 1100  $\text{cm}^{-1}$ , overlapping with the C—C stretching band of PVC. A decrease of band intensity at 1100  $\text{cm}^{-1}$  sug-



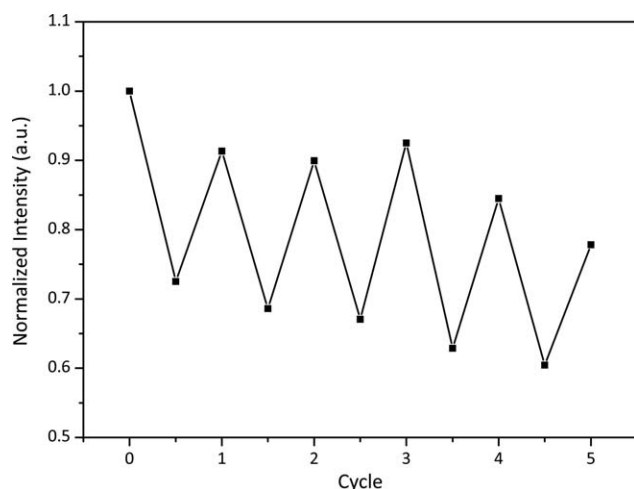
**Figure 7.** Responses of PVC-g-PS membranes to 1.0 mM solutions of various metal cations. ( $\lambda_{\text{Ex}}/\lambda_{\text{Em}} = 336/483 \text{ nm}$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

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



**Figure 9.** Fluorescence intensities of PVC-g-PS membrane after alternate treatment by solutions of  $\text{Fe}^{3+}$  and  $\text{Na}_2\text{EDTA}$ . ( $\lambda_{\text{ex}}/\lambda_{\text{em}} = 336/483 \text{ nm}$ ).

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  $\text{Fe}^{3+}$  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 mM aqueous solutions of  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Ag}^+$ . Figure 7 revealed that the membrane was capable of determining  $\text{Fe}^{3+}$  ions with a high selectivity over other metal ions.  $F_0/F$  values for  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Ag}^+$  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  $\text{Fe}^{3+}$  was also studied. Similar  $F_0/F$  values in Figure 8 indicated that the binding of  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  solution and saturated  $\text{Na}_2\text{EDTA}$  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  $\text{Fe}^{3+}$  forms a stronger complex with  $\text{Na}_2\text{EDTA}$  than with pyrene, the reversibility could be obtained.

#### CONCLUSIONS

This work provides simple and efficient approaches to fabricate fluorescence quenching-based optical sensor for  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  over other selected metal ions with good reusability.

#### ACKNOWLEDGMENTS

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