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SYNTHESIS AND ELECTROSPINNING OF A NOVEL FLUORESCENT POLYMER PMMA-PM FOR QUENCHING-BASED OPTICAL SENSING

Xianyan Wang,[1] Soo-Hyoung Lee,[1] Bon-Cheol Ku,[1] Lynne A. Samuelson,[3,*] and Jayant Kumar[2,*]

Departments of [1]Chemistry and [2]Physics, Center for Advanced Materials, University of Massachusetts—Lowell, Lowell, MA 01854
[3]Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA 01760

ABSTRACT

This work presents the synthesis of a new fluorescent polymer and its applicability for optical sensing using the electrospinning technique for the fabrication of nanofibrous membrane sensors. A new fluorescent monomer was first synthesized by coupling reactions between methacryloyl chloride and a pyrene derivative, 1-pyrene butanol. Fluorescent polymers containing different ratios of pyrene were then obtained by the copolymerization of this monomer with methylmethacrylate using 2,2′-azobisisobutyronitrile as the initiator. These polymers show distinct and well-defined fluorescence that is characteristic of the pyrene chromophores. Quenching-based optical chemical sensors were then fabricated by the electrospinning technique. The preliminary results show that these sensors have an order of magnitude higher sensitivity to the target analyte 2, 4-dinitro toluene than sensors formed from continuous thin films. This is believed to be due to the higher surface area to volume ratio of the electrospun nanofibrous membranes. The quenching behavior follows

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Stern-Volmer bimolecular quenching kinetics. The synthesis, characterization, electrospinning fabrication, and sensing capability of these polymers are discussed.

Key Words: Electrospinning; Fluorescent polymer; Optical sensing

INTRODUCTION

Over the last decade, polymeric materials have gained tremendous interest in optical sensor applications due to their unique properties.[1] However, polymer materials alone are generally not active sensing materials in that their optical parameters cannot be influenced by the environment. Therefore, suitable fluorescence indicators, that are sensitive to analyte and thus exhibit changes in fluorescence intensity, are used as molecular recognition materials in polymeric sensors. In this work, pyrene methanol (PM) was chosen as the fluorescent indicator because of its large Stoke's shift, high quantum yield, high absorbance, excellent photostability, long lifetime and nontoxic nature.[2] Covalent attachment of the fluorescent indicator, pyrene methanol, to poly(methylmethacrylate) (PMMA) offers a novel fluorescent polymer with both excellent processibility and sensing properties.

Recently, the electrospinning technique has been found to be a promising approach for fabricating large surface area thin films for sensor applications.[3,4] Electrospinning is a process by which high static voltages are used to produce an interconnected membrane-like web of small fibers, with the fiber diameter in the range of 10–1000 nm. Electrospun nanofibrous membranes can have a surface area approximately one to two orders of magnitude higher than those found with continuous thin films. It is expected that this high surface area will provide improved sensitivity and fast response time in sensing applications.

In this paper, copolymers with different pyrene dye contents were first synthesized via the polymerization of the methylmethacrylate with a new pyrene monomer. Optical nanofibrous membrane chemical sensors were then fabricated by electrospinning these polymers. The synthesis, characterization, electrospinning fabrication and sensing response of these electrospun membranes to the target analyte 2,4-dinitro toluene are presented.

EXPERIMENTAL

Reagents

All chemicals for synthesis, sensor fabrication and sensing measurements were purchased from Aldrich and purified by the literature methods.[5]

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Polymer Synthesis (PMMA-PM)

Fig. 1 shows the scheme of the synthesis of the fluorescent monomer and copolymers. To prepare the monomer, 1-pyrene butanol (1 g) was dissolved in tetrahydrofuran (THF) (20 mL) with pyridine (2 mL) and a trace amount of 2,6-di-tert-butyl-4-methylphenol. Methacryloyl chloride (2 mL) was added to the solution at 0°C under nitrogen atmosphere. After 24 h, with TLC monitoring, the solution was poured into water and the precipitate was filtered. The obtained solid was extensively washed with water and ethanol and dried under vacuum. The feed ratio for the preparation of polymers is described in Table 1 and a typical procedure is as follows: 52.1 mg of the fluorescent monomer, 0.73 g of methylmethacrylate (MMA) and 12.5 mg (1 mol % to the total monomers) of 2,2′-azobisisobutyronitrile (AIBN) were dissolved in 5 mL of THF. The solution was thoroughly degassed by several freeze pump-thaw cycles and heated in a sealed ampoule at 65°C for 2 days. The solution was cooled and slowly poured with vigorous stirring into methanol to precipitate the polymer. After filtering, the product was washed with methanol and dried in a vacuum oven.

Sensor Fabrication

Electrospinning was used as a novel and facile method to fabricate optical chemical sensors. The spin-dope solution, which consisted of a 26%, by weight, solution of the copolymer, was dissolved in propylene glycol

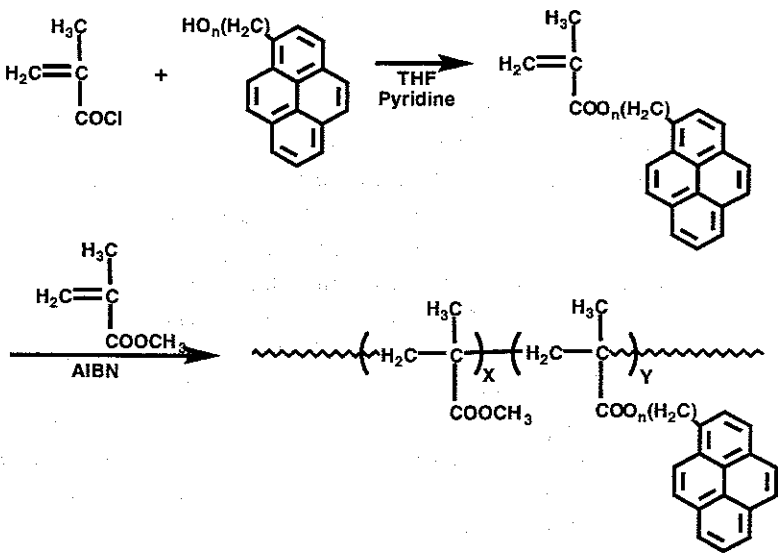

Figure 1. Synthetic scheme for fluorescent monomer and copolymer.

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Table 1. Feed Ratio for the Preparation of Polymers

	Feed Ratio (Mole %)
	Fluorescent Monomer/MMA
P1	1/99
P2	2/98
P3	4/96

methyl ether acetate. A live electrode wire from the DC power source was inserted into the pipette containing the spin dope. When the charge induced in the polymer solution overcame the surface tension of the liquid, a stream of polymer solution was produced. The solvent evaporated and very fine fibers were collected on a glass slide. The applied electrospinning voltages ranged from 15–20 kV. The working distance between the tip of the pipette and the glass slide was typically 15 to 20 cm. The collection time was about 30 to 45 sec. The electrospun membranes were dried in a vacuum oven at 70°C for 24 h. The sensing capabilities of the membranes were determined by measuring the fluorescence quenching with a fluorescence spectrofluorometer (SLM-AMINCO Model 8100). The electrospun membrane coated glass slide was fixed in a 1 cm quartz cuvette which was filled with analyte solution. The excitation wavelength was 336 nm. The emission spectra were measured from 315 nm to 410 nm.

RESULTS AND DISCUSSION

The fluorescent monomer used for the synthesis of the copolymers was prepared through the reaction of 1-pyrene butanol with methacryloyl chloride. The structure of the monomer was confirmed by NMR spectroscopy. The ^{13}C NMR spectrum in Fig. 2 shows a single peak at 167.5 ppm assigned to the ester carbon (*"c" from spectrum*). This ester group was also observed in the FT-IR spectrum (not shown) at 1739 cm^{-1}, showing C=O stretching bands. To prepare copolymers that have different fluorescent monomer ratios, P1, P2 and P3, the reaction of fluorescent monomer and MMA using AIBN as an initiator in THF solvent was performed. Fig. 3 shows the ^{1}H NMR spectra of the polymers. From the spectra, the copolymer compositions could be determined by comparing integration values of the aromatic hydrogen in pyrene (*"d" from the spectra*) and hydrogen in $-OCH_3$ (*"c" from the spectra*) and are shown in Table 2 with molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by GPC.

All polymers show the distinct absorbance and fluorescence peaks at 344 nm and 385 nm respectably that are characteristic of the pyrene

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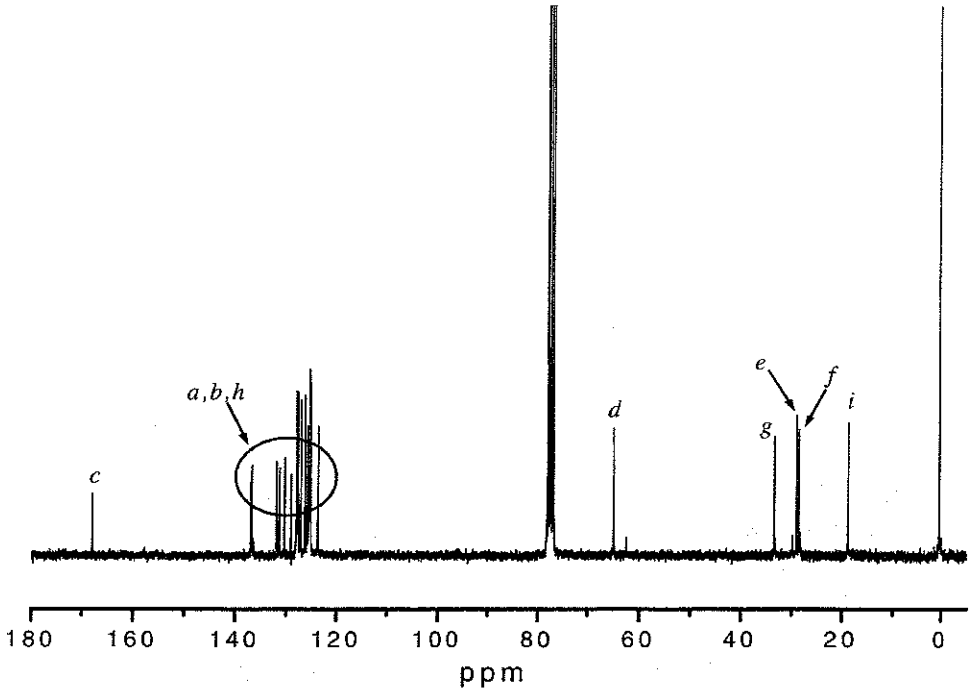

Figure 2. ^{13}C NMR spectrum of fluorescent monomer.

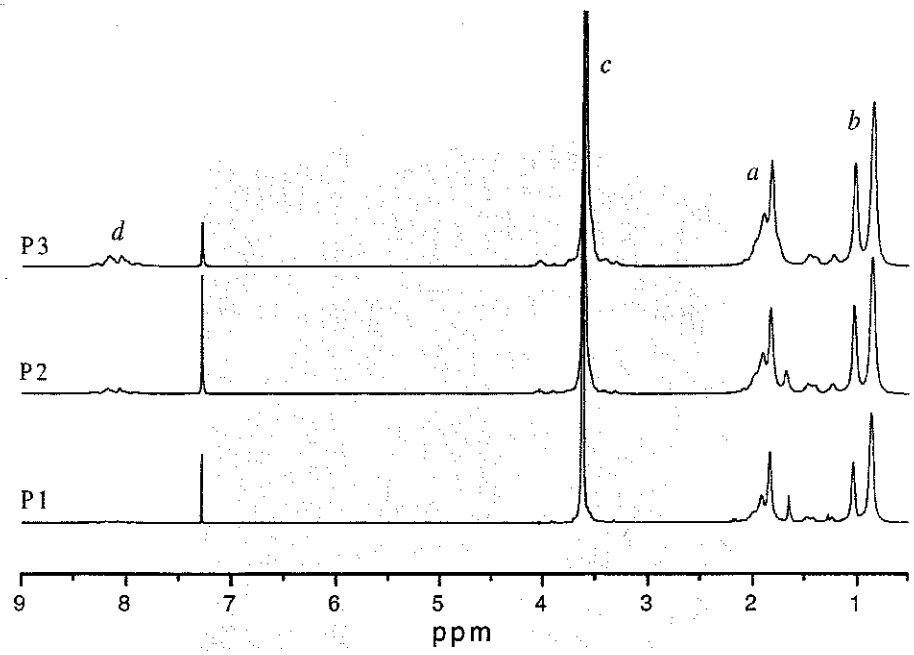

Figure 3. ^{1}H NMR spectra of copolymers.

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Table 2. Polymerization Results of Different Compositions

	Composition (Mole %)		
	Fluorescent Monomer/MMA	M_n	M_w/M_n
P1	0.78/99.22	59,545	1.560
P2	1.81/98.19	52,070	1.590
P3	3.77/96.23	49,110	1.718

chromophores. To investigate the sensing response of the polymers, the electrospun membranes were prepared on glass substrates and the intensities of the fluorescence as a function of various concentrations of 2,4-dinitro toluene (DNT) were measured. The SEM image shown in Fig. 4 was obtained from the electrospun membrane of the polymer P1 and shows the fibrous structure of the electrospun membrane with a diameter ranging from approximately 0.3 to 1 μm. The quenching of fluorescence by organic nitro compounds has been previously used for developing DNT sensors. Seitz et al. reported that membranes containing a pyrene fluorescent indicator were efficiently quenched by DNT.[6] In this report, fluorescence spectra as a function of different concentrations of DNT were measured from the electrospun membranes of P1, P2 and P3. The fluorescence intensity of the P3 membrane decreased with DNT concentration and the degree of quenching depended on the amount of DNT, as shown in Fig. 5. Similar behavior was

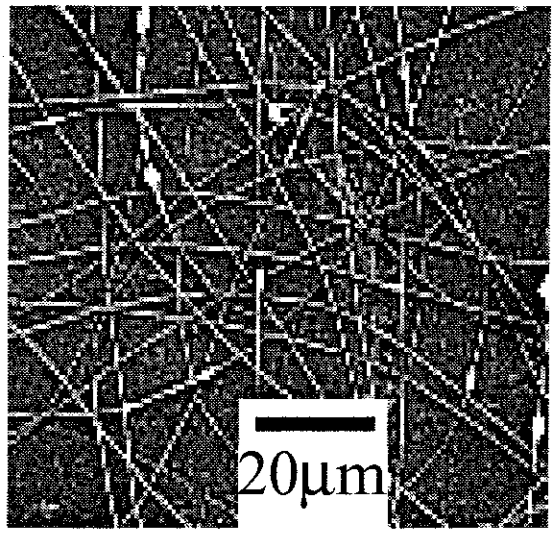

Figure 4. SEM image of an electrospun membrane.

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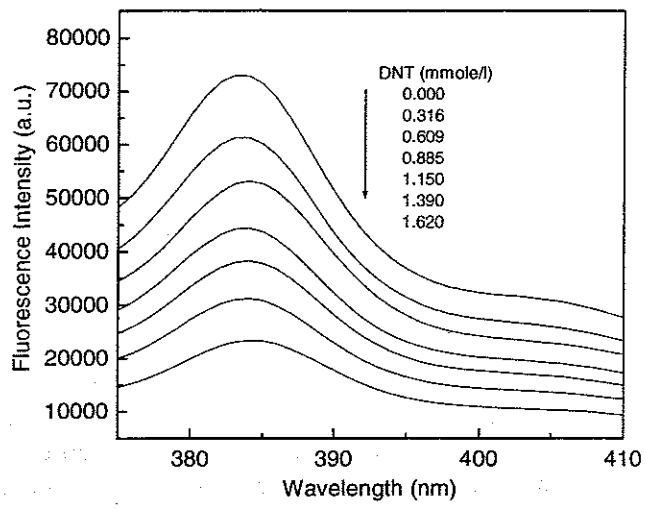

Figure 5. Fluorescence emission spectra of P3 electrospun membrane with varying DNT concentration.

observed in the polymers P1 and P2. The inset picture shows that the relative fluorescence intensity (I/I_0) decreases with DNT concentration.

The data obtained by performing a Stern-Volmer analysis (Eq. (1)) in polymers P1, P2 and P3 were plotted in Fig. 6. Linear relationships between

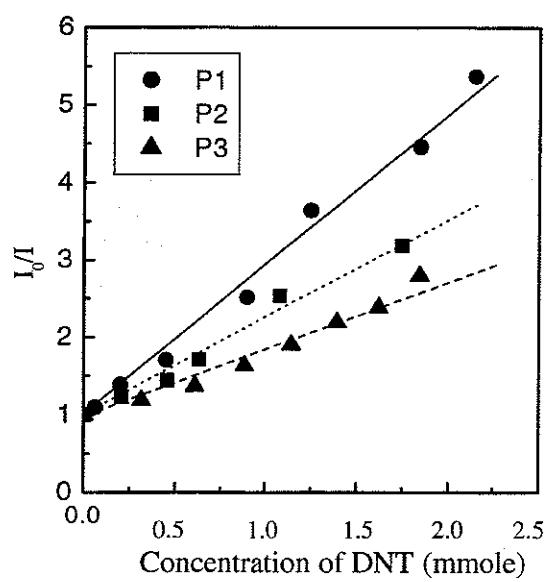

Figure 6. Stern-Volmer plots of electrospun membrane with varying DNT concentration.

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Table 3. Comparison of the Stern-Volmer Constants (K_{sv}) of the Polymers

	K_{sv} ($L\,mol^{-1}$)
P1	2.05×10^3
P2	1.42×10^3
P3	9.76×10^2

concentration of quencher (DNT) and I_0/I were obtained. Stern-Volmer constants (K_{sv}) were calculated from the slopes of each plot and are given in Table 3. These values are one order of magnitude higher than those obtained from continuous films of the similar polymer system by electrostatic layer-by-layer self-assembly (ELBL) technique, which were previously reported from our group.[7] We believe that this enhancement of the K_{sv} value is attributed to the higher surface area of the nanofibrous electrospun membranes. As mentioned before, increasing the surface area to volume ratio of the sensing film can increase the rate of quenching and enhance the K_{sv} value. It is also interesting to note that a higher value of K_{sv} was observed in the polymer P1 which contained a lower concentration of fluorophore. This may be explained in that the change of the fluorescence intensity due to small amount of quencher is more significant if the fluorescence intensity without quencher is lower. Therefore, a lower concentration of fluorophore should be advantageous to increasing the sensitivity of the sensor.

CONCLUSION

New fluorescent polymers were synthesized by radical polymerization and used for fabricating electrospun optical sensors for the detection of DNT. Electrospun nanofibrous membranes show higher sensitivities than conventional continuous thin films. A lower concentration of fluorophores in the sensor allows for more efficient quenching and higher sensitivities.

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