Effect of film thickness, blending and undercoating on optical detection of nitroaromatics using fluorescent polymer films

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ARTICLE INFO

ABSTRACT

In this work, using a fluorescent poly(phenylene ethynylene) containing the rigid pentiptycene and large cholesteryl ester pendent groups, the fluorescence quenching properties of the polymer thin films in response to vapor of 2,4-dinitrotulene (DNT) have been investigated by varying the film thickness, applying an undercoating and blending with another polar polymer. A significant change in fluorescence intensity (51% in 60 s) in response to DNT vapor exposure at ambient temperature was achieved when the polymer film coated on glass plate was about 2 nm in thickness. In comparison with the film of polymer alone, the film undercoated with (3-aminopropyl)triethoxysilane and the film of polymer blend containing a non-fluorescent polymer showed additional 18.5% (in 20-s exposure) and 18.7% (in 5-min exposure) decrease in fluorescence intensity, respectively. The use of polymer or polymer blend coated on optic-fiber tip for detection of DNT vapor has also been demonstrated.

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1. Introduction

Trace detection of explosives typically involves collecting vapor or particulate samples and analyzing them with various instruments. Currently, among many different techniques known for explosive detection, metal detectors and ion mobility spectrometry must be calibrated frequently; [1–3] whereas some methods are highly sensitive but are either expensive or require time-consuming procedures, such as surface enhanced Raman spectroscopy, mass spectrometry and energy dispersive X-ray diffraction [4–8]. Being different from these instrumental sensing systems, chemical sensors are molecular transducers that are able to detect a specific class of explosives, such as 2,4,6-trinitrotoluene (TNT) [9,10]. Sampling of this explosive is fairly difficult because TNT has extremely low vapor pressure (8.02×10^{-6} mmHg) at room temperature. Therefore, the detection of more volatile 2,4-dinitrotoluene (DNT, 1.47×10^{-4} mmHg at 22 °C), which is present in TNT, serves the purpose of explosive detection [11].

The Swager group reported a series of fluorescent, pentiptycene-containing conjugated polymers as chemosensors for detection of a trace amount of nitroaromatics and the detailed studies on the quenching mechanism and various effects (e.g., film thickness) on the sensing performance [12–15]. The extended conjugation along polymer backbone allows for efficient exciton migration and the large cavity in polymer traps the analyte molecules that effectively cause the fluorescence quenching. The bulky, rigid pentiptycene moieties can prevent interchain π-stacking and self-quenching of fluorescence of polymers in the solid state. We previously reported a series of highly sensitive sensory polymers containing the pendent cholesteryl ester groups for detection of nitroaromatics [16]. The pendent cholesteryl ester groups are believed to play a similar role as the pentiptycene moiety and pendent long alkyl chains of imparting the free volume and solubility to the polymers. Rapid and large response to DNT vapor with these polymer films coated on both glass plate and optic-fiber tip have been demonstrated.

Since the fluorescence signaling process involves the interaction between the target gas molecules and the solid polymer film, the sensing performance also depends on other materials' properties in addition to the intrinsic properties of a given polymers (e.g., free volume, fluorescence quantum yield and chain polarity). Adsorption of the gaseous analyte on the surface of a sensory polymer film and diffusion through the film are closely related to some sensing parameters such as response time, sensitivity and selectivity. A high diffusion rate for a specific analyte could lead to fast, large response (e.g., fluorescence quenching) in detection. However, low adsorption of the analyte could result in a slow response time or low

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sensitivity. Thus, chemical structure, morphology (e.g., porosity) and composition of polymer films should play an important role in the overall sensing performance. The presence of electron-rich groups such as amine in sensory polymer films should favor adsorption by electron-deficient nitroaromatic compounds. Considering the diffusion process of the analyte through a polymer film, the thickness and morphology of films can affect the sensitivity and selectivity.

The objective of this work is to probe the effect of the polymer film thickness and composition on detection of nitroaromatics, using a typical conjugated poly(phenylene ethynylene) (**P1**, Scheme 1) that could represent a class of potential sensory polymers. Experimentally, we explored the use of a thin layer of (3-amino-propyl)triethoxysilane (APTES) as either top-coating or undercoating for the sensory polymer film, varied the thickness of polymer film, and blended polymer **P1** with a polar polymer (polystyrene-maleic anhydride copolymer, PSMA). Vapor-phase detection of DNT was demonstrated using the optimized formulation on glass plate and then on the optic-fiber tip.

2. Experimental section

2.1. General methods

^{1}H NMR and ^{13}C NMR spectra were taken on a Burker Advanced Digital NMR 300 spectrophotometer, and chemical shifts are reported in ppm relative to TMS. Mass spectrometry was done with the Micromass Quattro LC ESI at the University of Ottawa. Infrared spectroscopic measurements were performed on a Varian 1000 FT-IR Scirnitar. The apparent molecular weights of selected polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform at ambient temperature at a flow rate of 1.0 mL/min; a UV detector set at 254-nm wavelength was used for detection. Inherent viscosities were measured in chloroform solution at 30 °C using an Ubbelohde dilution viscometer. Thermal stability of the polymer was determined using a Thermogravimetric Analyzer (TGA) 2950 CE Instrument at a heating rate of 10.0 °C/min. Polymer films on glass plates (microscope slide, 20 × 20 × 1 mm) were spin-coated using a Chemat Technology Spin-Coater KW-4B, with a spin-rate of 1500 rpm from chloroform solution, and dried in air overnight before use. To make a 10-nm thick film, 1 mg of polymer in 10 mL of chloroform is usually required. The polymer films on optic-fiber tips were dip coated from the polymer solution (0.5 mg/mL in chloroform) and dried in air. The film thickness was measured by the Nanosurf EasyScan Atomic Force Microscopy (AFM). The UV–vis spectra were recorded using a Lambda 900 spectrophotometer. The fluorescence sensing studies were done using a Shimadzu RF-1501 spectrofluorophotometer. The fluorescence spectra of polymer thin films were recorded by front-face (34° angle) detection. Fluorescence quantum yield in chloroform was determined relative to quinine sulfate (Φ_F = 0.53 at λ = 366 nm in 1N H$_2$SO$_4$). The absolute quantum yield of polymer film was measured using an integrated sphere.

2.2. Materials

The two monomers for making **P1**, dicholesteryl 2,5-dibromo-terephthalate and pentiptycene diacetylene, were prepared as reported before [16,17]. Polystyrene-maleic anhydride copolymer (Mw = 1900 with 75 wt% of polystyrene) was purchased from Aldrich Canada Inc. The solvents and reagents were purchased from Aldrich Canada Inc. and used without further purification.
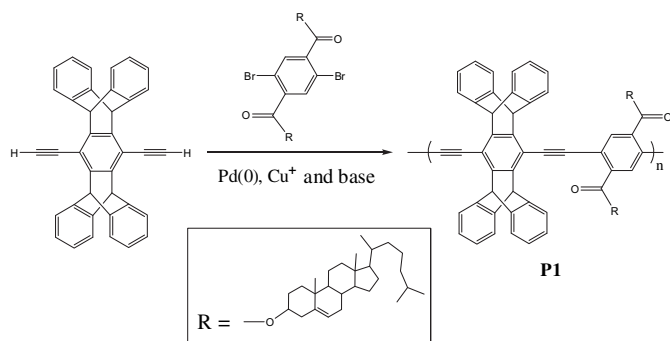
2.3. Polymerization

Under an atmosphere of argon, diacetylene monomer (0.1243 g, 0.260 mmol), dibromide monomer (0.2759 g, 0.260 mmol), Pd(Ph$_3$)$_4$ (0.040 g, 0.0344 mmol) and CuI (0.040 g, 0.212 mmol) were added to a 25 mL, two-necked round-bottomed flask, followed by addition of anhydrous toluene/diisopropylamine (3:2 v/v, 10 mL). The mixture was purged with argon for another 10 min and then heated at 65 °C for 3 days. The reaction mixture was diluted with CHCl$_3$ and washed with water at least 3 times. The organic phase was further washed with aqueous NH$_4$Cl solution twice and then dried over anhydrous MgSO$_4$. The solvent was removed in vacuo and the residue was reprecipitated in methanol three times. The resulting polymer was collected and dried in vacuo (0.350 g, 87.5% yield). IR (film, cm^{-1}): 2203 (C≡C), 1724 (C=O, ester), 1458 (C=C); ^{1}H NMR (300 MHz, CDCl$_3$): 8.48 (s, 1H), 7.19 (m, 8H), 6.88 (m, 8H), 5.37 (m, 2H), 5.19 (s, 4H), 3.99 (m, 2H), 2.55–0.9 (m, 90H); ^{13}C NMR (75 MHz, CDCl$_3$): 165.9, 145.7, 144.1, 140.8, 126.7, 123.7, 120.9, 99.3, 95.4, 93.3, 80.9, 73.7, 49.7, 37.4, 23.2.

3. Results and discussion

3.1. Synthesis and characterization

Based on Swager's and our previous work, we chose a fairly standard fluorescent polymer as a sensory material in this study (**P1**, Scheme 1), since the polymer design is not a main objective in this work. **P1** has the conjugated phenylene-ethynylene backbone and bulky pentiptycene and large cholesteryl ester pendent groups, which can prevent chain stacking and impart the solubility to the polymer. The pentiptycene moiety is incorporated in a diacetylene monomer, while the cholesteryl esters come from the corresponding dibromo monomer [16]. By the Sonogashira cross-coupling of these two monomers, **P1** was obtained in 90% yield. The chemical structure of **P1** was verified by NMR and IR spectroscopic methods. The IR spectrum exhibits a characteristic carbonyl band at 1716–1734 cm^{-1} ^{1}H and ^{13}C NMR assignments of **P1** were done with the aid of COSY and HETCOR experiments (see supporting information). Because of signal overlapping in the aliphatic region, only the vital peaks for its identification were assigned. **P1** is highly soluble in common organic solvents, such as chloroform, toluene and tetrahydrofuran, owing to large cholesteryl ester groups. The apparent weight-average molecular weight was determined by gel permeation chromatography (GPC) to be 1.0×10^5 relative to polystyrene standards (Table 1). In addition, high viscosity (0.92 dL/g) and good film-forming ability also indicate its high molecular weight. Thermal stability of polymer **P1** was characterized by thermogravimetric analysis (TGA). The decomposition temperature (Td) was above 288 °C in nitrogen, which is thermally stable enough for its use in a sensor at ambient temperatures. The glass transition

Scheme 1. Synthesis of **P1** by the Sonogashira cross-coupling reaction.

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Table 1
Characterizations of polymer P1.

Mw (Mw/Mn)	η_{inh} (dL/g)[a]	T_d (°C)[b]	Abs λ_{max} (nm)	PL λ_{max} (nm)[e]	Φ_F
1.0×10^5 (3.0)	0.92	288	429[c], 453[d]	453[c], 478[d]	0.68[c], 0.30[d]

[a] Inherent viscosity in chloroform at 30 °C.
[b] Onset temperature for 5% weight loss in nitrogen, as assessed by TGA at a heating rate of 10 °C/min.
[c] Measured in chloroform.
[d] Measured as a thin film (5 nm thickness).
[e] Excitation at 390 nm.

temperature (T_g) was not observed up to 290 °C by differential scanning calorimetry before the polymer began to decompose.

The absorption and fluorescence spectra of **P1** were taken in chloroform solution and as film (Fig. 1 and Table 1). The polymer has a strong absorption band at 429 nm which arises from π–π^* transition and strong blue-green fluorescence at 453 nm in solution (Fig. 1). A small red shift ($\sim$24–25 nm) in absorption and fluorescence was observed for the polymer film. The absorption and emission spectra for **P1** in solution and as thin film are quite similar. Such a small red shift and spectral similarity strongly suggest that interchain interaction in the solid state is much diminished due to the presence of large pendent groups but not completely. Absolute fluorescence quantum yield of polymer film was measured by using an integral sphere and found to be 30%, lower than that (68%) in dilute solution. The lower efficiency is likely due to self-quenching of the aggregates in the solid state.

In a fiber-optic sensing system, the polymer needs to be coated on the tip of optic fiber. Thus, the emission spectra were then compared for the films coated on glass plate and on optic-fiber tip. The slightly broader peak in the PL spectrum was observed for the film coated on optic-fiber tip (Fig. 2) but deemed not to affect the sensing experiments. Therefore, any changes in the fluorescence signals of polymer upon exposure to explosive analyte can be detected using an optic-fiber probe, in principle similar to the spectroscopic method using the polymer-coated glass plate.

3.2. Effect of polymer film thickness

The thickness of polymer film relates to the time for analyte molecules to diffuse into the entire film, which in turn relates to the number of energy traps available in the polymer film or the fluorescence quenching response of a given sensory polymer film.
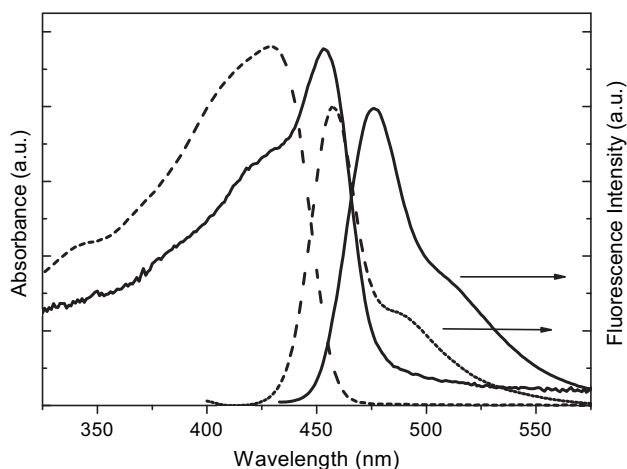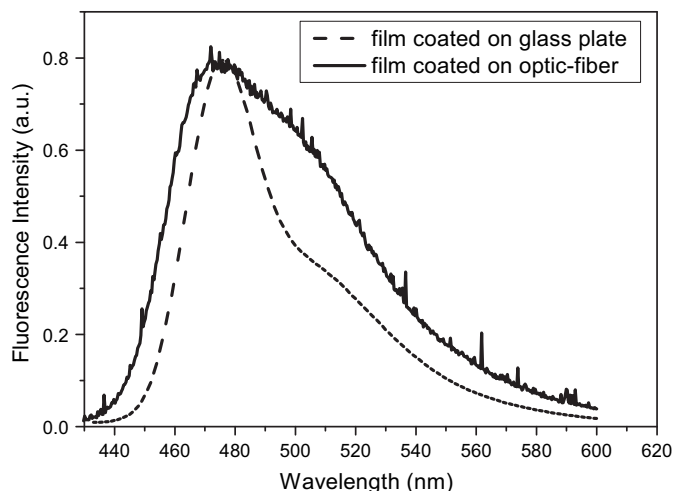

Fig. 2. Fluorescence spectra of P1 film coated on glass plate (dash line, excited at 390 nm) and optic-fiber (solid line, excited at 370 ± 20 nm).

Therefore, it is important to study and optimize the thickness of polymer film for sensing.

Films of polymer **P1** in thickness from ca. 2–70 nm were spin-coated on glass plates from chloroform solution in different concentrations and then subjected to the PL quenching tests under the same environmental conditions. The fluorescence quenching response (FQR) is defined as $\Delta PL\% = (I_0 - I)/I_0 \times 100\%$, where I_0 and I are the fluorescence intensity prior to and after exposure to analyte (DNT) vapor, respectively. The FQR at different time to the same analyte are shown in Figs. 3 and 4. For a 2–3 nm film, the FQR at 30-s exposures was 35.3%; however, it reduced to only 10.3% with a film in 58–62 nm thickness. The similar results were obtained at all the other time intervals within 60-s exposure to DNT vapor, especially in the first 30 s. Thinner films give a higher FRQ, which indicates that the fluorescence from the most polymers in a thinner film can effectively be quenched by DNT molecules than in a thicker film within 60 s. The film thickness of 2–3 nm was found to be optimal in our case for sensing with the largest FQR (e.g., 15–52%) and the shortest time (e.g., 10–60 s). A similar trend could be found within 1–5 min of DNT exposure as well (Fig. 4). However, after 5 min of exposure to DNT, films around 5–25 nm
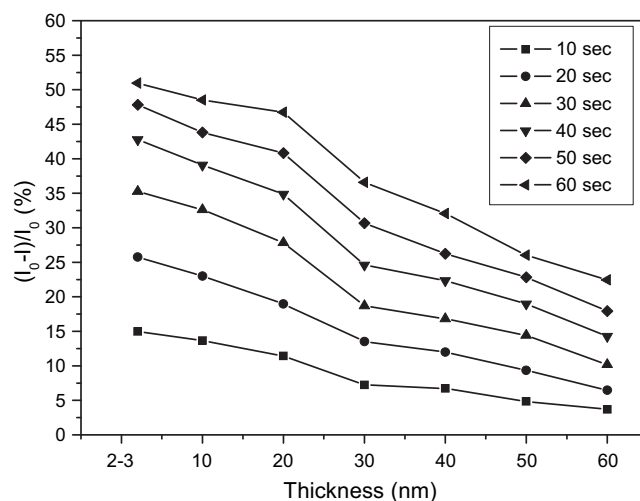

Fig. 1. Absorption and fluorescence spectra of P1 in chloroform (dash lines) and film coated on glass (solid lines).

Fig. 3. Fluorescence quenching response of films of P1 in different thickness after 10–60 s of exposure to DNT vapor.
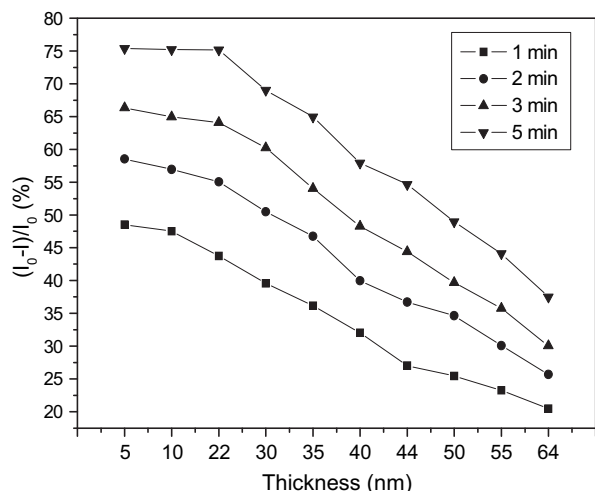
Fig. 4. Fluorescence quenching response of films of P1 in different thickness after 1–5 min of exposure to DNT vapor.

thickness gave almost the same FQR (75.1–75.5%), which means that the concentration of analyte molecules in the film, regardless the film thickness, has reached the equilibrium. For a thick film, because of the limited distance of diffusion of analyte in a short time there is always a layer of film close to the substrate whose fluorescence can not be quenched, and as well the large FQR which may offer a high detection sensitivity is in trade-off with a long detection time (>5 min). Therefore, it is desirable to use a thinner film for sensing nitroaromatic vapor.

Given that the thinner film gives the larger FQR, the sensing experiments were carried out using **P1** films coated on glass plate at room temperature in order to probe the scope and limitations of the FQR over time. Polymer film was exposed to the vapor of DNT solid, which was placed at the bottom of 50 mL vial and covered with cotton at room temperature. The fluorescence spectra of the polymer films were recorded immediately after exposure for a specific time, at the excitation wavelength of 390 nm. Fig. 5 shows the time-dependent fluorescence intensity of thin film (5 nm) of **P1** upon exposure to DNT vapor. The fluorescence intensity dropped 48.5%
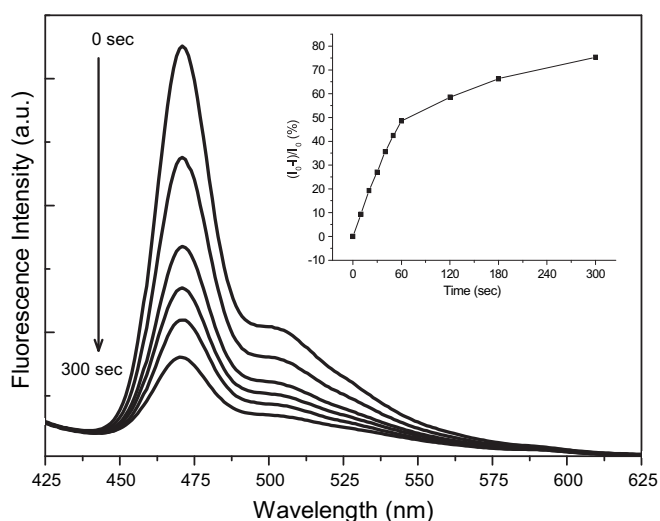

Fig. 5. The time-dependent PL spectra (excitation at 390 nm) of P1 film (5 nm) upon exposure to DNT vapor at room temperature at 0, 30, 60,120, 180 and 300 s. Inset: Fluorescence quenching response vs. time.

Table 2
Change in fluorescence quenching response of **P1** films (5–20 nm thickness) on glass plate with and without APTES undercoating[a].

Time Exposure to DNT	10 s	20 s	30 s	60 s
Change in FQR (%)	10.9	18.5	16.3	13.0

[a] Change in FQR = $\Delta a - \Delta g$, where Δa is the FQR with APTES undercoating and Δg is the FQR without undercoating.

after exposure to DNT for 60 s and the FQR seemed to reach a maximum of 75.4% after 300-s exposure to DNT vapor.

3.3. Effect of undercoating layer

The concentration of analyte molecules in sensory polymer film or the actual amount of analytes that can remain in the polymer depends on the interaction between the polymer and analyte and can directly affect the fluorescence quenching. The polar electron-donating groups such as amino tend to bind the electron-deficient nitroaromatic compounds well through the electron donor and acceptor interaction, which deems to attract and trap the analyte molecules, leading to effective quenching. Thus, it is conceivable that the addition of the amino-containing component into a sensory polymer can help 'fix or trap' the nitroaromatic in the sensory film and thus increase the analyte concentration or enhance the FQR. A variety of amino compounds could be selected and tested. (3-Aminopropyl)triethoxysilane (APTES) is a surface promoter and can form an ultrathin layer of coating with the free amino groups on the surface of a variety of substrates such as glass, silicone and plastics. In our work, APTES was spin-coated on the glass plate from its 2% solution in toluene, and heated at 120 °C for 10–15 min to form a thin layer of undercoating (7.5–8.5 nm). The **P1** films were then spin-coated on the APTES-treaded glass plates. The films were even and smooth and gave the same optical properties as those without the APTES undercoating. The PL quenching data were collected as an average of six films with the 5–20 nm thickness coated on glass plates with and without the APTES undercoating (Table 2). In comparison, the polymer films with the APTES undercoating gave a better FQR than those without the undercoating. On average, a noticeable increase (10–18%) in FQR was achieved within 10–60 s. This improvement in detection sensitivity can be attributed to the presence of the amino-containing undercoating that is able to absorb and hold more DNT molecules in a sensory film for PL quenching. The **P1** thin films with the APTES top-coating and thick films of **P1** with the APTES undercoating were also tested. Both did not give any meaningful enhancement in the FQR. For a thick film, the PL quenching is still determined by the diffusion process of the analyte and there is no or very little interaction between the APTES coating and the analyte molecules. With the APTES top-coating, although the analyte might be adsorbed readily onto the film surface but still goes through the same diffusion path into the film as the one without the APTES top-coating, making no difference in the overall FQR. Therefore, the amino-containing undercoating can

Table 3
Increase in fluorescence quenching response of polymer blend films relative to P1 film on glass plate.

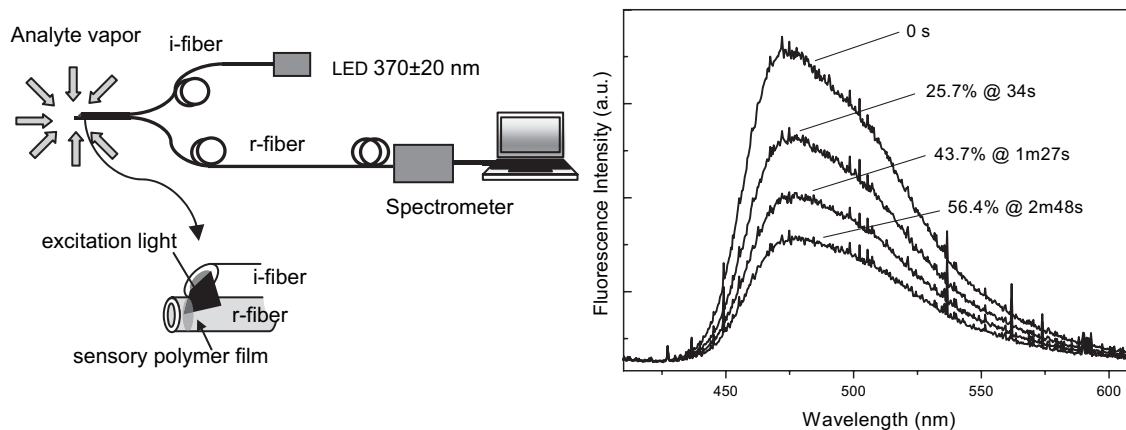| Δ FQR (%)	Blend film (40–50 nm)		Blend film (50–60 nm)
Time (min)	P1:PSMA (1:1)	P1:PSMA (3:1)	P1:PSMA (3:1)
1	4.2	8.8	23.6
2	6.0	16.8	27.5
3	7.8	16.8	24.1
5	6.8	18.4	18.7

Fig. 6. (A) Left: a schematic drawing of an experimental setup for fiber-optic sensing of explosives; i-fiber is an illuminating fiber and r-fiber is a receiving fiber, which is dip-coated with sensory polymer. (B) Right: Fluorescence quenching response of **P1** film (ca. 30 nm) coated on optic-fiber tip.

serve as a sorbent by absorbing and holding the DNT molecules in the sensory film, which effectively enhances the sensing sensitivity.

3.4. Effect of polymer blending

By diluting a fluorescent polymer in solution or another non-fluorescent polymer, the fluorescence quantum yield may increase due to the diminished interchain interaction. At the same time, if the non-fluorescent polymer is able to facilitate the mobility of the analyte molecules to diffuse into the polymer film, blending it with a sensory polymer should give a higher FQR towards the analytes. There are a vast number of polymers that could be selected for blending tests. Ideally, commercially available polymers should be selected for blending with polymer **P1** for potential practical application. Among many possible candidates, PSMA was selected and tested, which is a copolymer of styrene and maleic anhydride. The polar anhydride and aromatic phenyl groups in PSMA are deemed to be able to interact with the DNT molecules. Three polymer blends were prepared in weight ratios of **P1**:PSMA as 3:1, 1:1 and 1:3. The polymer blends were spin-coated on glass plates from their chloroform solutions. The fluorescent quenching response of the films of the blends and polymer **P1** in the same thickness was measured and compared. The results showed a noticeable improvement in detection sensitivity (Table 3). After 2 or 3-min exposure to DNT, the FQR was 16.8% larger for the blend films (3:1 by weight, 40–50 nm thickness) than the **P1** film alone. A larger increase (27.5%) in the FQR for the thicker films (50–60 nm) of polymer blend (3:1 by weight) further indicates the effect of blending with a polar polymer. The best results in terms of the FQR came from the blend with the weight ratio of 3:1 for **P1** and PSMA. The other two blends in ratios of 1:1 and 1:3 were found to give less or no increase in the FQR.

3.5. Fiber-optic sensing study

The experimental setup for fiber-optic sensing of DNT vapor was reported previously [16]. Compared with the spectroscopic method for explosive detection using the film coated on glass plate, the optic-fiber detection is more sensitive and is capable of remote sensing. The fiber probe consists of the two fibers that bind together with one fiber serving for excitation light delivery and the other for fluorescent signal collection. Polymer film is dip coated on the receiving fiber and the fluorescence signal can efficiently transport to the monitor with the minimum loss from the environment. However, this sensing system requires a minimum level

of fluorescence and relatively smooth films for detection reliability. The optimal thickness (e.g., 5 nm) found for the polymer film coated on glass plate did not work well for the optic-fiber probe, due to the limitation of the required fluorescence signal. The APTES undercoating was not applied in order to simplify the coating process. It was then found that the film of polymer **P1** in 30-nm thickness is able to afford a fluorescence signal large enough for fiber-optic measurement. As shown in Fig. 6, the fluorescence intensity gradually decreases over time upon exposure to DNT vapor. A detectable change in signal or FQR of 25.7% was recorded after exposure to DNT vapor at room temperature for only 34 s. The 56% drop in fluorescence was achieved after 2m48s. The optic-fiber detection using the blend of **P1** and PSMA also worked well. The fiber probe coated with blend film (**P1**:PSMA = 3:1 by weight, 75 nm thickness) was able to detect the DNT vapor with the FQR of 12.2% at 5 min.

4. Conclusion

The fluorescence quenching properties of the polymer thin films in response to DNT vapor have been investigated by varying the film thickness, applying an undercoating of APTES and blending with PSMA. Thinner films show a larger signal response to DNT vapor. A significant change in fluorescence intensity (51%) in response to 60-s exposure to DNT vapor was achieved with the 2-nm thick polymer film coated on glass plate. The APTES undercoating can enhance the detection sensitivity, as an additional 11–19% increase of the FQR was observed with 5–20 nm thick films. The films of P1-PSMA blend also showed noticeable improvement in DNT detection, which provided additional 19% (in 5-min exposure) increase in the FQR. The use of polymer and polymer blend coated on optic-fiber tip for detection of DNT vapor has also been demonstrated.

Appendix. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2010.01.003.

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