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A polydiacetylene multilayer film for naked eye detection of aromatic compounds

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ABSTRACT

A blue-colored polyelectrolyte multilayer (PEM) film of poly(10,12-pentacosadiynoic acid), or poly(PCDA) vesicles, was successfully prepared by layer-by-layer deposition with polycationic chitosan, and its application as a colorimetric chemo-sensor for water soluble aromatic compounds was investigated in comparison to the same poly(PCDA) vesicles as a liquid sol. The color of the PEM film changes from blue to red within 5 min when immersed into 10 mM α-cyclodextrin (α-CD) solution giving the colorimetric response (CR) of ~65%. The α-CD induced color transition of the PEM film was completely inhibited in the presence of 10 mM of either benzoic acid or 4-nitrophenol, which represents a 1:1 mole ratio of aromatic compound:α-CD, showing nearly zero percent CR and the film remained blue. In contrast, only partial inhibition was observed by eyes in the presence of 20 mM 4-methoxyphenol and indole as the film appeared purple with ~15% CR. Phenol and nitrotoluene did not show inhibition detectable by naked eyes but the low level of inhibition, ~35% CR remained, was observed spectroscopically at 20 mM. For nitrophenols, the degree of inhibition is varied by the isomeric structures in the following order: 4-nitrophenol > 3-nitrophenol > 2-nitrophenol. The competitive inclusion of the aromatic compound into the α-CD cavity is probably responsible for the observed inhibition of color transition. Compared with the liquid sol of poly(PCDA) vesicles, the PEM film, as a solid sol, offers less color interference from turbidity and intrinsic color of the samples being analyzed that the results of inhibition can be readily justified by naked eyes.

1. Introduction

Colorimetric detection that is clearly observable by the naked eye is highly desirable for on-site analyses of toxic substances. Polydiacetylene (PDA) is one of the most successful polymeric materials currently being developed as colorimetric indicators for temperature [1–8], chemicals [9–14] and biological agents [15–25]. The external stimuli generally disturb the side chain packing that affects the electronic absorption of the ene-yne conjugated backbone of PDA, resulting in its color transition from either blue to red or red to yellow [26–29].

The color transition of PDA from blue to red in contact with α-cyclodextrin (α-CD) solution was observed for the first time in a Langmuir–Schaefer (L–S) film prepared from PDA containing an aniline head group [30]. This color transition can be inhibited by 4-nitrophenol (4-NP) by competitive formation of an inclusion complex with the α-CD. Subsequent research has confirmed that α-CD has an effect on the formation and color change of PDA vesicles by insertion of the PDA head group into the cavity of α-CD [31,32]. The sensitivity of each type of PDA has not been specifically addressed in the literature reports. Nevertheless, the concentration of α-CD used for the induction of color transition of PDA containing a carboxylic head group was reported to be significantly lower than that of PDA containing an amide head group, implying the higher sensitivity of the former toward α-CD [30–32]. To expand the utility of the PDA-based chemo-sensors, fabrication of PDA in various forms has been reported. A micro-multichannel filled with PDA-embedded PEG hydrogel matrix has been prepared for the simultaneous analyses of multiple samples [33]. However, the gel-based device required a long detection time, in the range of an hour, and exhibited a low sensitivity which is probably due to the slow diffusion rate in the very viscous gel medium. In contrast, the L–S film revealed a higher sensitivity and a shorter detection time, but the fabrication of L–S film into naked eye detectable devices is technically demanding. Alternatively, polyelectrolyte multilayer (PEM) membrane interchanging electrostatic layer-by-layer assembly of

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cationic and ionic electrolyte become a powerful way to prepare multilayer thin film [34,35].We have recently reported a convenient method for the preparation of polyelectrolyte multilayer (PEM) films containing intact PDA vesicles using layer-by-layer deposition [36]. The color intensity of the film can be effectively controlled by the number of the vesicle layers deposited. In this article, the application of the PEM film containing poly(10,12-pentacosadiynoic acid), poly(PCDA), vesicles for detection of aromatic compounds in water is reported. As a solid sol, the PEM film exhibits a few benefits over the liquid sol of the vesicles.

2. Experimental

2.1. Materials

The diacetylenic monomer, 10,12-Pentacosadiynoic acid (97% (w/w) purity; PCDA), was purchased from Fluka, USA. Chitosan was purchased from Seafresh Chitosan (Lab) Company, Thailand. The viscosity-averaged molecular weight (M_v) was 8.0×10^5, and the degree of deacetylation determined by colloidal titration was 84%. Diethyl ether was purchased from Lab-Scan, Thailand. Generally, deionized water was used for reagent preparation and rinsing, except for the vesicle preparation where milli-Q water with a resistance of 18.1 MΩ was used. All other solvents and chemicals were analytical or reagent grade purchased from Fluka and used as received without further purification, unless specified otherwise.

2.2. Preparation of poly(PCDA) vesicles

PCDA was dissolved in diethyl ether and the solvent was evaporated by purging with N_2. After the addition of milli-Q water, the PCDA suspension (0.5 mM) was sonicated by using a 230 W bath sonicator (Ultrasonicator, Elma, Germany) for 20 min at 75–85 °C. The resulting colloid was kept at 4 °C overnight before the temperature was then brought up to room temperature and polymerized by UV irradiation at 254 nm for 5 min to yield a blue sol of poly(PCDA). The blue-colored poly(PCDA) vesicle sol was filtered through 1/125 mm filter paper to remove any undesired lipid aggregates.

2.3. Preparation of chitosan solution (the polycationic solution)

The chitosan powder (0.5 g) was dissolved in 1.0 mL of glacial acetic acid and diluted to 100 mL with deionized water. The solution was stirred at room temperature for 12 h to allow the complete dissolution and diluted again with water to make a total volume of 500 mL (0.1%, w/v). The solution was centrifuged to discard any insoluble polymer and the clear solution was collected.

2.4. Preparation of chitosan/poly(PCDA) multilayer film

A chitosan/poly(PCDA) multilayer film was prepared in accordance with the published method [36]. The pH of the poly(PCDA) and chitosan solutions were adjusted within the range of 3.0–3.3 by using HCl (0.1 mM). A clean glass slide, used as a substrate, was dipped in the chitosan solution for 5 min and then rinsed by deionized water three times. The glass slide was then dipped into the poly(PCDA) sol for 5 min, rinsed again three times and then dipped into the chitosan solution to form another layer. The dipping and rinsing cycle was repeated until the film with desired color intensity was obtained.

2.5. Colorimetric measurements

The colorimetric response (CR) was used to quantitatively evaluate the blue-to-red transition which is generally determined and reported in percentage (%CR). The %CR is $100 \times (PB_0 - PB)/PB_0$, where PB is the percent blue calculated from $A_{blue}/(A_{blue} + A_{red})$. The A_{blue} and A_{red} were the absorbance of the blue and red phases of poly(PCDA) measured at λ_{max} around 635 and 540 nm, respectively. The initial percent blue (PB_0) was determined on the samples before exposure to the stimulus.

2.6. Study of color transition induced by α-cyclodextrin

A chitosan/poly(PCDA) multilayer film was introduced into a quartz cuvette filled with the deionized water (pH 6.0, temp = 25 °C) and allowed to stand for 5 min before an electronic absorption spectrum was taken. The spectra were collected from 800 to 400 nm with the absorbance at 800 nm set to zero. The procedure was repeated after replacing the water with α-cyclodextrin (α-CD) solutions, the concentrations of which were varied from 0 to 20 mM. At each concentration, a film/solution contact time of 5 min was allowed prior to spectrum acquisition. The color transition of the vesicle liquid sol was studied in comparison to the film by mixing a fresh sol of poly(PCDA) vesicles (A_{635} = 0.15–0.20) with α-CD solution at each concentration tested and the absorption spectrum was acquired.

2.7. Study of inhibition of color transition by aromatic compounds

An aqueous solution of α-CD (10 mM) was mixed with each tested aromatic compound, i.e. phenol, 2-, 3- and 4-nitrophenol, 4-nitrotoluene, 4-methoxyphenol, benzoic acid and indole, at various concentrations (0–20 mM) and sonicated for 2 min. Starting from the solution containing the highest concentration of the aromatic compound, the PEM film was dipped into the solution for 10 min. The film was then withdrawn from the solution and dipped into a quartz cuvette filled with deionized water and the absorption spectrum was collected from 800 to 400 nm. The same film was

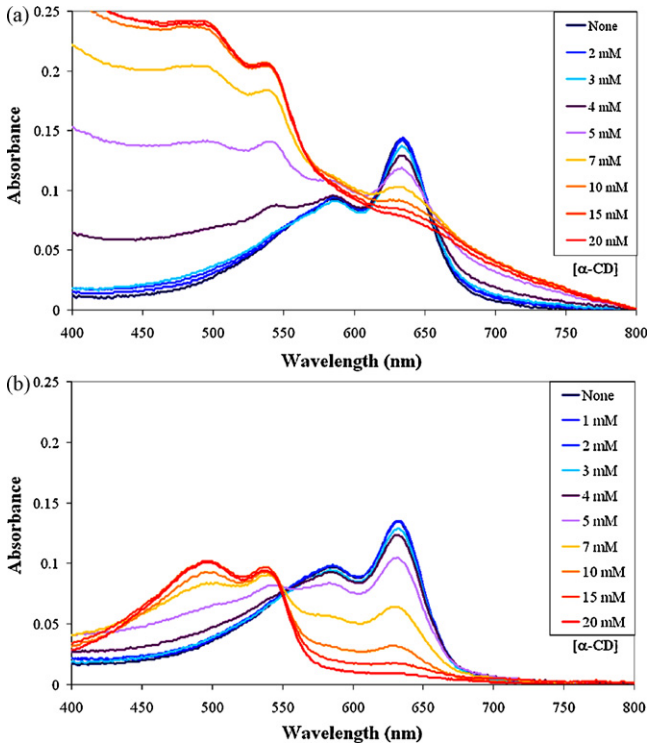

Fig. 1. Electronic absorption spectra of poly(PCDA) vesicles recorded at 25 °C and 5 min after the addition of various concentrations of α-CD solution into liquid sol (a), and the 10-layered PEM film (b).