



Dual colorimetric response of polydiacetylene/Zinc oxide nanocomposites to low and high pH



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ABSTRACT

This contribution presents our continuation work on the color-transition behaviors of polydiacetylene(PDA)/ZnO nanocomposites prepared by using three types of monomers, 5,7-hexadecadiynoic acid (HDDA), 10,12-tricosadiynoic acid (TCDA) and 10,12-pentacosadiynoic acid (PCDA). The color-transition behaviors of these nanocomposites upon exposure to acid and base are investigated by utilizing UV/vis absorption spectroscopy. We have found that these PDA/ZnO nanocomposites exhibit colorimetric response at both low and high pH regions. The addition of acid causes the poly(HDDA)/ZnO, poly(TCDA)/ZnO and poly(PCDA)/ZnO nanocomposites to change color from blue to red at pH ~ 5, 3.5 and 2, respectively. The color of pure PDA vesicles, on the other hand, is hardly affected at this pH range. At high pH region, the pure poly(TCDA) vesicles change color at pH ~ 8 while it requires much higher pH to induce color transition of the PDA/ZnO nanocomposites. The mechanism responsible for color transition of the PDA/ZnO nanocomposites is explored by various techniques including infrared spectroscopy, zeta potential analyzer and light scattering. Our result provides a new approach for controlling the colorimetric response to pH of PDA-based materials.

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1. Introduction

Sensing materials based on colorimetric response are highly desirable due to the simplicity of their utilization. Conjugated polymer is a class of sensing materials that have received considerable attention from scientific communities over the past few decades. Polydiacetylene (PDA) in particular has been extensively investigated and utilized in various advanced sensing technologies [1–10]. It has been observed that PDA exhibits drastic color change upon exposure to various external stimuli such as solvents [11–16], surfactants [17–20], temperature [6,7,12,21–29], ions [30–35], acids and bases [12,36–44].

PDA is normally prepared via topopolymerization process. In aqueous medium, diacetylene (DA) monomers, constituting polar head and long alkyl tail, tend to assemble into vesicular structure at suitable condition [6–8]. Topopolymerization of the organized

DA monomers is achieved by UV light or γ -ray irradiation without the need of chemical initiators or catalysts. Under normal condition, PDAs generally display a deep blue color with $\lambda_{\max} \sim 640$ nm and vibronic shoulder at ~ 590 nm. Although many research groups have investigated color-transition behaviors of the PDAs [7,12,25,45–49], the responsible mechanisms are still not fully understood. However, it has been generally accepted that the disturbance of external stimuli alters molecular conformation such as side chain and backbone packing of the PDAs. These structural changes affect the electronic states of conjugated backbone, resulting in the widening of HOMO–LUMO energy gap (i.e. blueshift of the absorption band). Magnitude of the blueshift varies with PDA structures and strength of the perturbation by external stimuli.

It has been known that some types of PDAs change color upon varying pH. The development of PDA-based materials for sensing acid or base, however, receives rather limited attention. Common PDA molecules normally constitute a carboxylic head group and an alkyl side chain. This type of PDA exhibits irreversible blue to red color transition upon increasing the pH [12,38]. The addition of hydroxide ion (OH^-) removes acidic protons from the carboxylic heads, breaking hydrogen bonds at the vesicle surface. Moreover, this acid–base reaction also converts the carboxylic head to negatively charged carboxylate. The strong ionic repulsion between the carboxylate groups and the breaking of hydrogen bonds causes

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segmental rearrangement of the PDA, resulting in the color transition. The decrease in pH does not cause any color transition but instead induces agglomeration at relatively low pH value [38,50].

The colorimetric response of PDAs to pH can be controlled by structural modification. Early works by Cheng and Stevens demonstrate that the color transition occurs at different pH values when the head groups of PDA are modified with various types of amino acids [36]. In some cases, the modified PDAs exhibit color transition in acidic pH region. Recently, Seo and Kim fabricate PDA assemblies from a series of N-(n-aminoalkyl)-10,12-pentacosadiynamide [42]. In this system, the presence of amino head groups allows acid–base reaction with various types of acid, which in turn induces color transition of the PDAs. The change in alkyl spacer between amine head and amide group affects the extent of color transition. They suggest the utilization of these modified-PDAs for sensing warfare gases. Recent study by one of the authors observes that the length of alkyl side chain also affect colorimetric response to pH of the PDA [12]. Although the structural modification of PDAs is the most effective method for controlling their color-transition behaviors, it normally requires complicate synthetic route, expensive chemicals and a time consuming purification process. These are major problems in mass production for the industrial scale utilization.

Recently, our research group presents a simple method for fabricating PDA/ZnO nanocomposites [21,22]. The strong ionic interaction between carboxylate head and positively charged group at the surface of ZnO nanoparticles limit segmental dynamics of the PDA. This results in the increase in color stability when subjected to external stimuli. Interestingly, the PDA/ZnO nanocomposites exhibit reversible thermochromism [21]. We also demonstrate that the shortening of PDA alkyl side chain in the nanocomposites leads to a systematic decrease in their color-transition temperatures [22]. In this continuation work, we observe that these PDA/ZnO nanocomposites show dual colorimetric response upon exposure to acid or base. The color transition also takes place at different pH values depending on structure of the constituent PDA. Three types of DA monomers, 5,7-hexadecadiynoic acid (HDDA), 10,12-tricosadiynoic acid (TCDA) and 10,12-pentacosadiynoic acid (PCDA) are used for preparing PDA/ZnO nanocomposites. Our system provides new type of PDA-based materials for sensing acid and base. We propose new mechanism responsible for color transition of this class of materials.

2. Experimental

The DA monomers used in this study, HDDA, TCDA and PCDA, were commercially available at Fluka. The ZnO nanoparticles with diameter in a range of 20–200 nm [21] were purchased from Nano Materials Technology (Thailand). PDA/ZnO nanocomposites were prepared as followed. The DA monomers were dissolved in chloroform and then filtered using 0.45 μm pore size nylon membrane to remove polymerized materials. The solution was heated at about 80 °C to evaporate the chloroform. The ZnO nanoparticles were dispersed in deionized water by using probe sonication for 10 min. The aqueous suspension of ZnO was added into the purified DA monomers. The concentration of DA monomers was 1 mM while the ZnO/DA ratio was kept at 10 wt.% in all experiments. The suspensions were sonicated at about 80 °C for 60 min to co-disperse the DA monomers and ZnO nanoparticles into aqueous medium. The self-assembling of DA monomers on ZnO nanoparticles was allowed to take place by keeping the suspensions at ~ 4 °C for ~ 24 h. Topopolymerization of the nanocomposites was carried out by irradiating with ordinary UV light ($\lambda \sim 254$ nm, 10 W) for 1 min, yielding the aqueous suspensions with blue color. The pure PDA

vesicles were prepared by using the same procedure but without adding the ZnO nanoparticles.

Absorption spectra were measured by using Analytik Jena Spectord S100. The pH of PDA vesicles and the nanocomposites was adjusted by addition of NaOH or HCl solutions. To quantify the extent of blue to red color transition, the CR values were calculated according to the equation, $\text{CR} (\%) = [(PB_0 - PB)/PB_0] \times 100$. The PB values were calculated from $A_{640}/(A_{540} + A_{640})$, where A_{540} (red) and A_{640} (blue) were the absorbance at 540 nm and 640 nm, corresponding to the amount of red and blue phases, respectively. Since the absorption peaks of poly(HDDA)/ZnO nanocomposite in blue phases were detected at 660 nm, we used the absorbance at 660 nm (A_{660} (blue)) for the calculation of CR values.

FT-IR spectra of pure PDA vesicles and PDA/ZnO nanocomposites were obtained using a Perkin Elmer Spectrum GX spectrometer in transmittance mode. The samples were prepared by mixing dried PDAs vesicles or PDA/ZnO nanocomposites with KBr powder and pressed into pellets. Zeta potential and size distribution of PDA vesicles and the nanocomposites were measured by Brookhaven, ZetaPaLs. Morphologies of PDA vesicles and the PDA/ZnO nanocomposites upon variation of pH were investigated by scanning electron microscopy SEM (JEOL, JSM-6400). Samples for SEM measurements were prepared by drop casting from aqueous suspensions onto a polished silicon wafer.

3. Results and discussion

3.1. Colorimetric response to pH

In previous studies, the color-transition behaviors of pure poly(PCDA) and poly(TCDA) vesicles are normally investigated in high pH region [12,38]. For comparison purpose in this study, we explore the system of pure poly(TCDA) vesicles in both low and high pH regions. Absorption spectra of aqueous suspension of poly(TCDA) vesicles measured upon decreasing and increasing pH are shown in Fig. 1. In low pH region, the addition of H^+ ions hardly affects the color of vesicles. The absorption pattern remains roughly the same at pH ~ 2.5 . The further decrease in pH causes a growth of small shoulder at ~ 550 nm, corresponding to slight change in the suspension color. An incubation of the vesicles at this pH region causes precipitation. Previous study observed the aggregation at pH value lower than 4 when the vesicles were incubated for a few hour [38]. In our study, the poly(TCDA) suspension was continuously stirred for a few minutes prior to the measurement. Therefore, the aggregation of vesicles was minimal, indicated by relatively strong absorbance.

In the basic condition, an irreversible blue to red color transition of poly(TCDA) vesicles occurs upon increasing the pH. A peak of red phase at ~ 546 nm grows significantly when the pH is above 8. At this stage, the added OH^- ions abstract carboxylic protons of the head groups causing a systematic increase in the negatively charged carboxylate. When strong ionic-repulsive force between the carboxylate groups overcomes the dispersion interaction between the alkyl tails, the rearrangement of poly(TCDA) segments occurs. The color transition completes at pH ~ 10 where absorption spectra constitute peak and shoulder at ~ 546 nm and ~ 505 nm, respectively. The pure poly(PCDA) vesicles exhibit similar color-transition behavior. However, the color transition takes place at slightly higher pH compared to that of the poly(TCDA) due to the stronger attractive dispersion interaction between the alkyl tails [12].

The PDA/ZnO nanocomposites show rather different color-transition behaviors when exposed to acid and base. The absorption spectra of poly(PCDA)/ZnO nanocomposite measured upon decreasing pH are illustrated in Fig. 2a. Interestingly, color of the

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