THE COLORIMETRIC RESPONSE TO pH OF POLYDIACETYLENE/ZnO NANOCOMPOSITES

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Abstract: Polydiacetylene vesicles (PDA) are conjugated polymers that exhibit the unique color-transition property when expose to external stimuli such as temperature, pH, solvents and mechanical stress. They have much attention for utilized as active materials in sensing applications. The preparation of polydiacetylene vesicles in the form of nanocomposites with metal oxides is a simple technique to tailor their colorimetric response. Addition of metal oxides results in ordered arrangement of 10,12-pentacosadiynoic acid (PCDA) monomers on the metal oxide surface. The polymerization is carried out by UV irradiation. In this work, we study the colorimetric response of pure PCDA vesicles compare to poly(PCDA)/ZnO nanocomposites in acid and basic conditions. The absorption spectra measured by UV-vis spectroscopy show that decreasing of pH rarely affect the color of pure PCDA while the poly(PCDA)/ZnO nanocomposites exhibits the color transition from blue to purple at pH 4.14. On the other hand, Adding of NaOH results in completely color changing of pure PCDA at pH 7.41. The poly(PCDA)/ZnO nanocomposites requires higher NaOH concentration for color changing. It exhibits the color transition from blue to purple at pH 13.28.

Introduction: Recently, The conjugated polymer has received an enormous attention for utilizing as a sensing material[1]. One of them is polydiacetylene (PDA) an amphiphilic molecule that consists of carboxylic head group and hydrophobic alkyl side chain. Spontaneous formation of PDA in water results in the vesicles structure with spherical shape and cavity in the center[2,3]. PDA vesicles can change the color form blue to red when apply the environmental perturbations such as changing of temperature[4], pH[5,6] , adding of solvents or biomolecules[7] and mechanical stress[8]. PDA vesicles can be easily prepared by dispersing the monomers in water using ultrasonic and kept in low temperature for self-assembly to bilayer structure. The polymerization is carried out by UV irradiation. The external stimuli cause the color transition by inducing the dynamic of alkyl side chains and then deformation of conjugated backbone. The distortion of conjugated backbone results in the decrease of conjugation length. The energy band gap between HOMO and LUMO is wider, causing electrons to absorb higher energy and, therefore, exhibits the color changing. The color transition mechanisms depend on the kind of perturbation.

Controlling the color transition property of PDA vesicles can be approached in many ways. The preparation of PCDA vesicles in nanocomposites with metal oxide is one option to tailor the colorimetric response. This procedure is easy and can be prepared in water that is low cost and environmental friendly. In addition, polymerization can be obtained by UV light without using any catalysts or initiators. Metal oxide acts as the nanosubstratefor PDA molecules to absorb and spontaneous assembly on its surface due to ionic interaction between carboxylic head group and the metal oxide surface charge. The interested metal oxides for preparation of nanocomposites with PDA are ZnO[9,10], TiO_2, SiO_2[11], Fe_3O_4, etc.

In this work, we aim to tailor the colorimetric behavior of 10,12-pentacosadiynoic acid or PCDA by formation of nanocomposites with ZnO. We study the colorimetric response to pH (acid and basic regions) of poly(PCDA)/ZnO nanocomposites compare to pure PCDA vesicles.

Methodology: 10,12-pentacosadiynoic acid or PCDA (Fluka) and ZnO nanoparticles (Nano Materials Technology, Thailand) are commercially available. The morphology and particle size distribution of ZnO nanoparticles were investigated by Transmission Electron Microscopy (TEM, Tecnai 12,D291) and laser light scattering (Malvern Mastersizer 2000), respectively. The PCDA/ZnO nanocomposites were prepared as followed. Purified PCDA was prepared in chloroform and then filtered through 0.45 µm nylon membrane to remove the aggregated materials. The chloroform was evaporated at ~50 °C and a dried film of purified PCDA was obtained. ZnO nanoparticles were pre-dispersed in deionized (DI) water by using ultrasonic probe for 5 min, and then added into purified PCDA at 10 wt%. The suspension was sonicated in ultrasonic bath at 75-80 °C for 30 min and then kept in refrigerator overnight for self assembling of PCDA monomer on ZnO surface. Polymerization was done by irradiated with UV light for 5 min to obtained the nanocomposites in deep blue color. Self-assembly and structure of poly(PCDA)/ZnO nanocomposites are shown in Figure 1. Pure PCDA vesicles can be prepared by the same method but without the step of adding of the ZnO aqueous solution. The initial pH of nanocomposites and pure PCDA vesicles in aqueous solution were about 6.5 – 6.9. The morphology of pure PCDA vesicles and poly(PCDA)/ZnO nanocmposites were observed by Scanning Electron Microscopy (SEM, LEO 1455 VP). The absorption spectra of pure PCDA vesicles and poly(PCDA)/ZnO nanocomposites upon addition of HCl and NaOH were measured by UV-Vis spectrophotometer (Specord S100B, Analytik Jena) to investigate the color transition behavior.

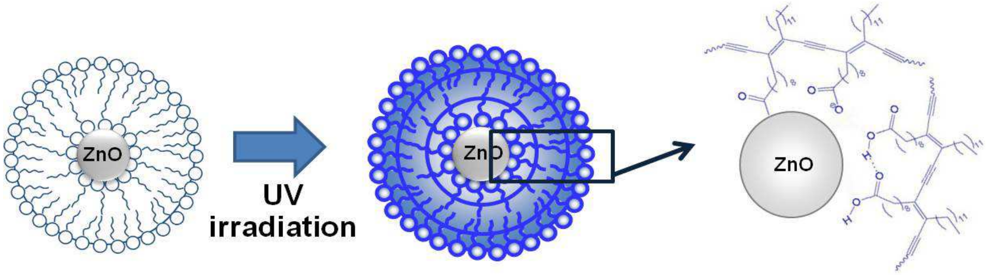

Figure 1. Self-assembly and structure of poly(PCDA)/ZnO nanocomposites

Results and Discussion:

Morphology and particle size distribution

Morphology of ZnO nanoparticles is investigated by TEM as shown in Figure 2(a). ZnO nanoparticles are agglomerate with size of 20-200 nm. The particle size distribution of ZnO nanoparticles is measured by laser light scattering as shown in figure 2(b). The result shows large size distribution with mean value of 0.162 µm. Morphology of pure PCDA vesicles and poly(PCDA)/ZnO nanocomposites are investigated by using SEM as illustrated in figure 3. Both vesicles and nanocomposites are almost spherical in shape. The diameters of pure PCDA vesicles range from 40 to 130 nm and, for the nanocomposites, the sizes are 50 to 450 nm.

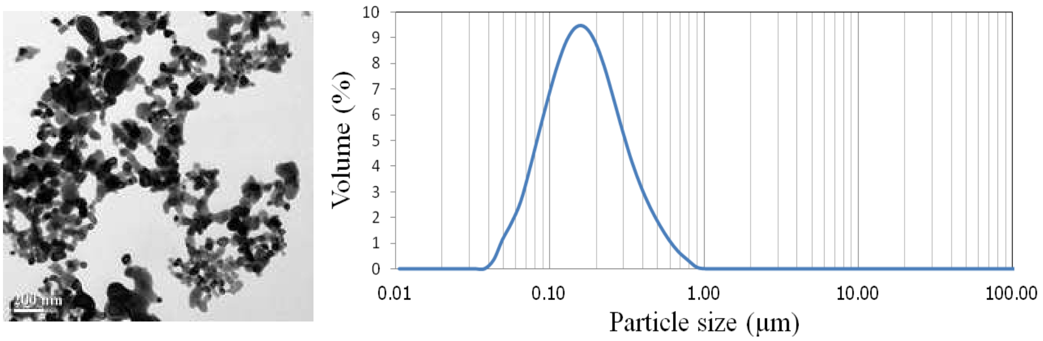

Figure 2. (a) TEM image of ZnO nanoparticles (b) Particle size distribution of ZnO nanoparticles

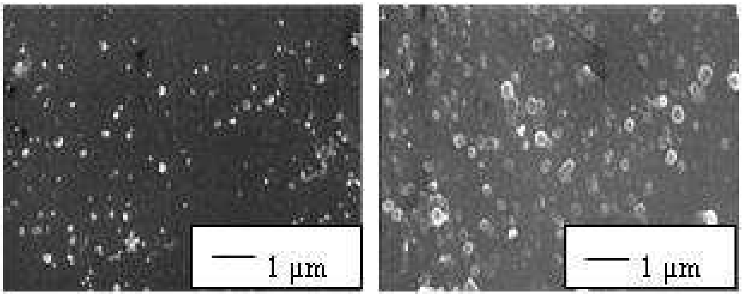

Figure 3. SEM images of (a) Pure PCDA vesicles and (b) poly(PCDA)/ZnO nanocomposites

Colorimetric response to pH

Acid condition

As shown in figure 4, irradiation by UV light causes the pure PCDA vesicles and poly(PCDA)/ZnO nanocomposites to exhibit the maximum absorption band or λ_{max} at 640 nm and vibronic shoulder at 590 nm, which designed as the blue form. The appearance of blue color indicates the polymerization of PCDA monomers or additional polymers in the system. The pH of pure PCDA vesicles and poly(PCDA)/ZnO nanocomposites in water are 6.88 and 6.94, respectively. The UV-Vis absorption spectra of pure PCDA vesicles measured upon addition of HCl are illustrated in figure 4(a). With decreasing pH, intensity of λ_{max} at 640 nm continuously decreases. The absorption spectra show slightly growth of 550 nm peak at pH 2.17 and lower, indicating the color change to purple. The colorimetric response of poly(PCDA)/ZnO nanocomposite suspension is different from pure PCDA vesicles. The absorption spectra in figure 4(b) clearly show strong effects of acidic pH on the nanocomposite suspension. Changes in absorption pattern of the nanocomposites can be observed at pH 4.14, in which the peak at 550 nm appears and then increase in intensity when pH decreases. The nanocomposite suspension finally appears red color.

The colorimetric response to acidic condition is summarized in Figure 5. The plot of %CR as a function of pH exhibits stronger effects of acidic pH on the nanocomposites comparing to pure PCDA vesicles. Color transition of the nanocomposites appears at lower HCl concentration. Moreover, %CR of the nanocomposites is higher than that of pure PCDA, indicating higher magnitude of color change from blue at initial state. The results may cause by high concentration of added protons (H^+) interact with the lone pair electron of oxygen ion in carboxylic head group, inducing the repulsive force between the adjacent positive ions.

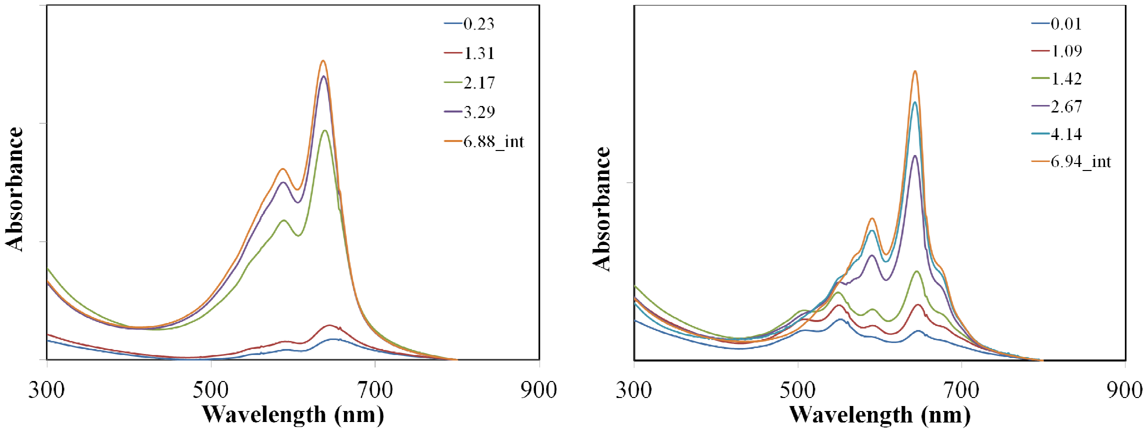

Figure 4. Absorption spectra of (a) Pure PCDA vesicles and (b) poly(PCDA)/ZnO nanocomposites in aqueous suspensions upon pH decreasing.

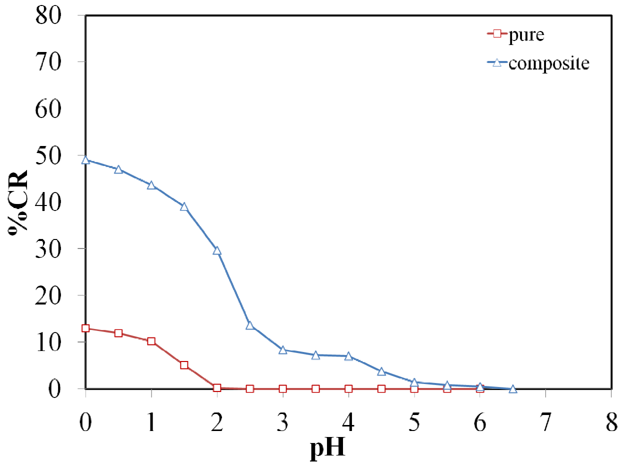

Figure 5. Plots of %colorimetric response (%CR) upon decreasing pH of (□) pure PCDA vesicles and (Δ) poly(PCDA)/ZnO nanocomposites

Basic condition

The colorimetric responses of pure PCDA vesicles and poly(PCDA)/ZnO nanocomposites in aqueous solution are shown in Figure 6. Slight addition of NaOH causes appearance of 550 nm peak in the spectrum of pure PCDA suspension at pH 7.41 (figure 6(a)) and the suspension exhibits purple color. The increase of pH leads to increasing in the 550 nm peak intensity. At pH 13.11, the absorbance peak at 640 nm disappears and the final color of the suspension is red. On the other hand, the addition of NaOH solution exhibits less effect on color transition of the nanocomposite suspensions (see Figure 6(b)). Higher NaOH concentration is required for color changing to take place. The peak at 550 nm is slightly observed at pH 13.28, in which the suspension turns to purple color. Corresponding %CR upon increasing of pH is shown in Figure7.It clearly shows strong effect of basic pH condition on color transition of pure PCDA vesicles.

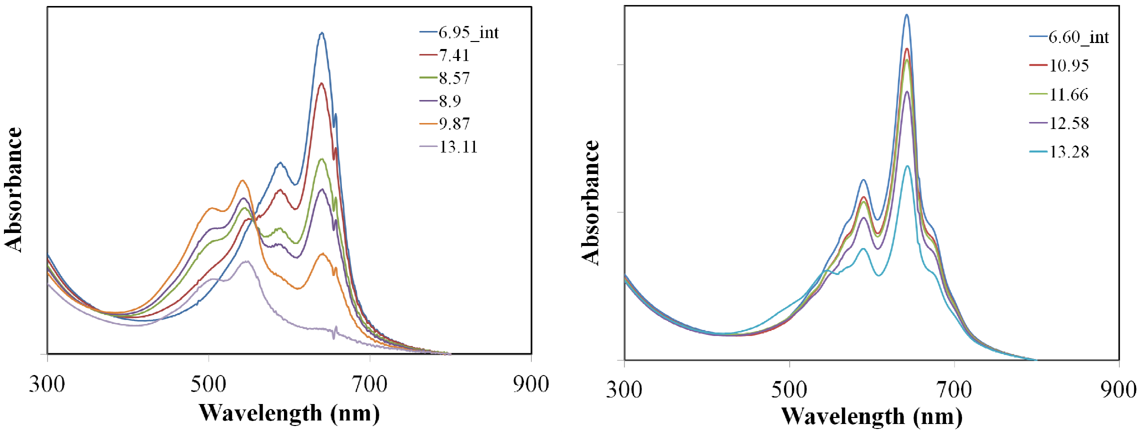

Figure 6. Absorption spectra of (a) Pure PCDA vesicles and (b) poly(PCDA)/ZnO nanocomposites in aqueous suspensions upon increasing pH.

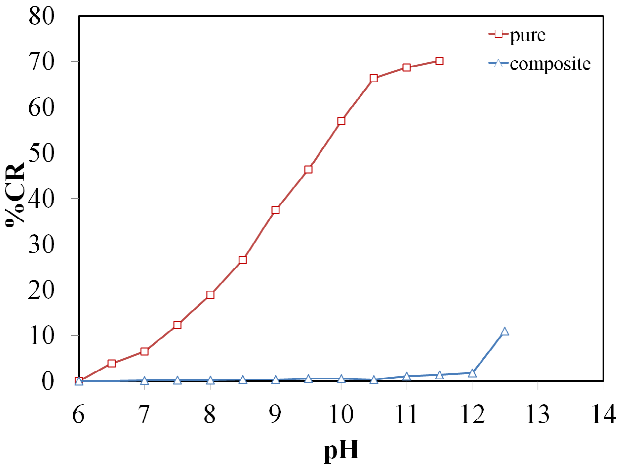

Figure 7. Plots of % colorimetric response (%CR) upon increasing pH of (□) pure PCDA vesicles and (Δ) poly(PCDA)/ZnO nanocomposites

The carboxylic head group of pure PCDA vesicles interacts with its neighbors by hydrogen bonding. In blue form, the side chains and the conjugated backbone are in ordered arrangement. The perturbation of PCDA vesicles by adding NaOH increases OH^- into the system. The OH^- ions attract proton from head group, breaking the hydrogen bonding and transforming carboxylic to carboxylate. The repulsive force between the negative charges causes the dynamic of side chains and induces the distortion of conjugated backbone. The vesicles in this stage appear red phase. This mechanism also occurs in the nanocomposites. However, strong ionic interaction between ZnO nanoparticles and the polymer stiffens the side chains and hinders distortion of conjugated backbone, resulting in difficulty in color transition.

Conclusion: A new class of PDA-based materials is successfully prepared by adding ZnO nanoparticles into the cavity of vesicles structure. The poly(PCDA)/ZnO nanocomposites exhibits different color transition behavior from pure PCDA vesicles. We found that addition of HCl into the pure PCDA suspensions results in slightly color changing while poly(PCDA)/ZnO nanocomposites changes from blue to purple at pH around 4.14. For basic condition, the absorption spectra show that increasing of pH strongly affects the color transition of pure PCDA vesicles. The suspension changes color from blue to red at pH 7.41. On the other hand, poly(PCDA)/ZnO nanocomposites require higher NaOH concentration for color changing. It exhibits the color transition at pH 13.28. This research presents a method of producing PDA-based materials and their colorimetric response, which expands their applications in sensing technology.

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