



# Role of $\text{Zn}^{2+}$ ion on the formation of reversible thermochromic polydiacetylene/zinc oxide nanocomposites



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## ABSTRACT

Polydiacetylene (PDA)/zinc oxide (ZnO) nanocomposite is a class of materials that exhibit reversible thermochromism with controllable color-transition temperature. The nanocomposite also changes color upon exposure to various types of acids and bases. In our continuing efforts to develop this material, we obtain evidences that reveal true nature of the nanocomposite formation. X-ray diffraction (XRD) technique detects a significant increase of the interlamellar distance within the nanocomposite comparing to that of the pure constituent PDA. The investigation of the nanocomposite systems prepared from 10,12-tricosadiynoic acid and 10,12-pentacosadiynoic acid provides consistent results. This indicates an intercalation of the  $\text{Zn}^{2+}$  ions, leaking out of the ZnO nanoparticles, between the PDA layers. An atomic absorption spectroscopy confirms the existence of  $\text{Zn}^{2+}$  ions in the aqueous solution. The XRD result also shows that using only  $\text{Zn}^{2+}$  ions to prepare the nanocomposite can provide the intercalated PDA/ $\text{Zn}^{2+}$  structure. However, the enhanced inter- and intrachain interactions within this system is not sufficient to provide reversible thermochromism. An infrared spectroscopy detects the variation of vibrational frequencies of carboxylate head groups within the systems of PDA/ZnO nanocomposite and PDA/ $\text{Zn}^{2+}$  assemblies, corresponding to different types of interactions. Therefore, the strong interfacial interaction between PDA head groups and ZnO nanoparticle is essential for obtaining the reversible thermochromism. We also attempt to prepare the nanocomposites by using a combination of  $\text{Zn}^{2+}$  ions and various types of substrates including  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  nanoparticles.

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## 1. Introduction

Thermochromic materials have been a subject of immense interest during the past few decades, mainly due to their potential utilization in various applications such as sensors and displays [1–4]. Polydiacetylene (PDA) is one of the most studied materials that typically changes color from blue to red upon increasing temperature [2–16]. The PDAs can also exhibit other types of color transition such as blue-to-purple, purple-to-red, red-to-orange, and blue-to-orange, depending on their architectures and/or temperature range. The color transition of PDAs is known to involve structural relaxation of their side chain and conjugated backbone [17–20]. The segmental rearrangement of PDAs results in electronic species, which absorb light at different regions. Therefore, the extent of thermal perturbation determines their colors at elevated temperature.

The PDA assemblies in aqueous suspension prepared from the commercially available monomers, 10,12-tricosadiynoic acid and 10,12-pentacosadiynoic acid, exhibit irreversible blue-to-red color transition at about 55 °C and 60 °C, respectively [8,21]. Structural modification of the PDAs can be utilized for controlling the color-transition temperature [5,6,12,14–16,21–25]. The shortening of alkyl tail normally leads to the decrease of color-transition temperature due to the weakening of dispersion interactions within the PDA assemblies [21,22]. The incorporation of head groups possessing strong interactions, on the other hand, provides an opposite result. In some cases, the color transition becomes reversible, which in turn extends their utilization in many applications [14–16,24,25]. Recent studies have demonstrated that the reversible thermochromism of PDAs can be achieved by incorporating various cations including  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Dy}^{3+}$  into the assemblies [18,20,26–29]. In these systems, the enhanced electrostatic interactions between these cations and the negatively charged carboxylate head groups allow structural relaxation back to the original state upon cooling to room temperature. The incorporation of cations can also add properties to the PDA systems. For examples, the chiral PDA film

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can be obtained via the coordination of  $\text{Cu}^{2+}$  ion with carboxylate head group of achiral PDA [20,30]. The green PDA with highly extended conjugation length is achieved by the addition of  $\text{Cd}^{2+}$  ion accompanied with thermal annealing at appropriate temperature [19]. The PDA/ $\text{Cs}^+$  assemblies exhibit color transition upon exposure to moisture due to the hygroscopic property of the  $\text{Cs}^+$  ion [26].

Our group recently introduces a class of materials by incorporating zinc oxide (ZnO) nanoparticles into PDA assemblies in order to control the color-transition behaviors of PDAs [10–11,31–34]. The diacetylene (DA) monomers are induced to assemble onto ZnO substrates via electrostatic interactions. The presence of strong interfacial interactions within this system facilitates high ordering organization of the DA monomers essential for the topotactic polymerization. The resultant PDA/ZnO nanocomposites exhibit reversible thermochromism in aqueous suspension and various organic solvents [10]. The color reversibility persists up to 200 °C for the PDA/ZnO nanocomposites that are fabricated into thin films by embedding in various polymeric matrices. Their color-transition temperature can be finely tuned by varying photopolymerization time and structure of the constituent PDAs [11, 32]. In addition, the PDA/ZnO nanocomposites exhibit dual colorimetric response to acids and bases, allowing their utilization as chemical sensors [33,34].

In our continuing efforts to develop this class of reversible thermochromic materials, we obtain evidences that reveal true nature of the formation of PDA/ZnO nanocomposites. Different techniques are utilized in this study including X-ray diffraction (XRD), atomic absorption spectroscopy, infrared (IR) spectroscopy, UV/vis absorption spectroscopy and zeta potential measurement. Our combined results indicate that  $\text{Zn}^{2+}$  ions leaking out of the ZnO nanoparticles play an essential role on the formation of PDA/ZnO nanocomposite. The nanocomposites prepared by using other types of nanoparticles,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , are also investigated.

## 2. Experimental

The DA monomers; 10,12-pentacosadiynoic acid (PCDA), 10,12-tricosadiynoic acid (TCDA), and the  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  nanoparticles used in this study were commercially available at Aldrich. The ZnO nanoparticles were purchased from Nano Materials Technology (Thailand). The preparation of poly(PCDA)/ZnO, poly(PCDA)/ $\text{SiO}_2$ , poly(PCDA)/ $\text{TiO}_2$  and poly(PCDA)/ $\text{Al}_2\text{O}_3$  nanocomposites followed the procedures described in our previous reports [31,32]. The concentration of PCDA monomer was 1 mM while the ratio of nanoparticle/PCDA monomer was kept at 10 wt% in all experiments. The preparation of poly(PCDA)/ $\text{Zn}^{2+}$  assemblies followed the same method. Concentrations of the added  $\text{ZnCl}_2$  (Aldrich, AR grade) were varied from 0.01 mM to 1 mM. Topotactic polymerization of the samples was carried out by illuminating with UV light (10 W,  $\lambda \sim 254$  nm) for 5 min, resulting in blue suspensions.

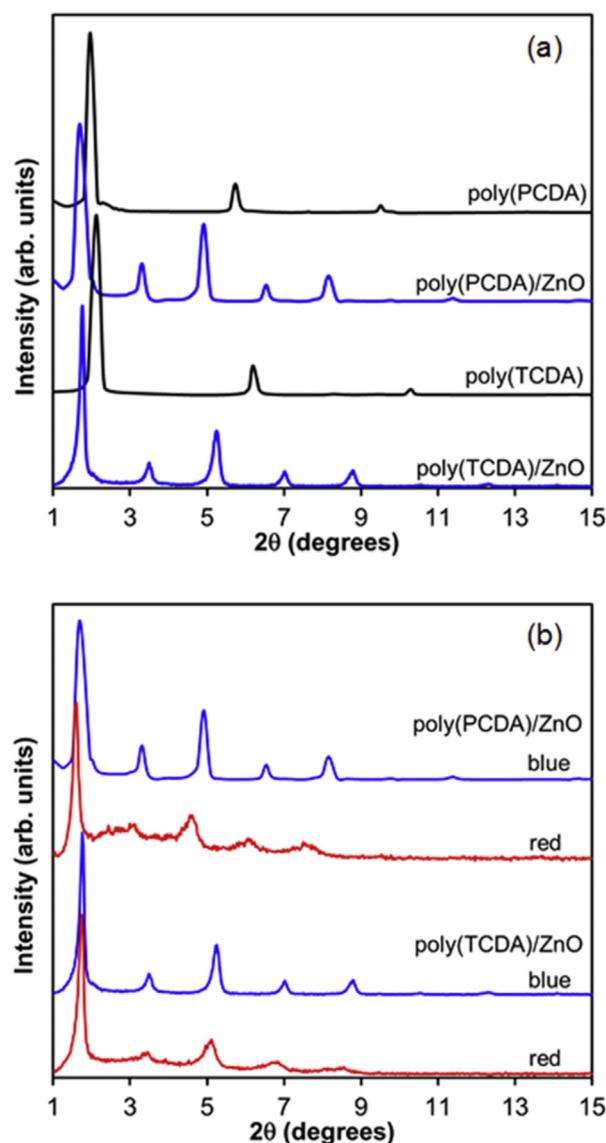
The structures of poly(PCDA)/ZnO, poly(TCDA)/ZnO nanocomposites, pure poly(PCDA) and pure poly(TCDA) in blue and red phases were investigated by using XRD method (Bruker AXS Model D8 Discover,  $\lambda(\text{Cu}_\alpha) = 1.54$  Å). The measurement was carried out using vertical configuration and theta/theta geometry. The blue phase samples were prepared by drop casting onto glass slides. The red phase was obtained by annealing the samples in a vacuum oven at 200 °C for 30 min. The XRD results of blue and red phase PDAs were obtained from the same sample. Absorption spectra of pure PDAs and the nanocomposites in aqueous suspensions were measured by using Analytik Jena, Specord S100. Zeta potential of the metal oxide nanoparticles in aqueous suspensions were measured by Brookhaven, ZetaPals. Fourier transform infrared (FT-IR) spectra were obtained using Nicolet 6700 FT-IR spectrometer in transmittance mode. The dried samples were mixed with KBr powder and pressed into pellets. The concentration of  $\text{Zn}^{2+}$  ions leaking from ZnO nanoparticles was measured by using atomic absorption spectroscopy (Perkin Elmer, AAnalyst 200 with S10 autosampler).

$\text{ZnCl}_2$  was used to prepare standard solutions with known concentration of  $\text{Zn}^{2+}$  ions. The ZnO nanoparticles were dispersed into aqueous suspension by ultrasonication following the same steps used for preparing the nanocomposites. However, the DA monomers were not added into the system. The suspensions were centrifuged at 35,000 rpm for 30 min to precipitate the ZnO nanoparticles. The resultant supernatants containing  $\text{Zn}^{2+}$  ions were analyzed.

## 3. Results and discussion

### 3.1. Structure of the PDA/ZnO nanocomposites

The XRD patterns of poly(PCDA), poly(TCDA), poly(PCDA)/ZnO and poly(TCDA)/ZnO nanocomposites in thin films are illustrated in Fig. 1a. A previous study of pure poly(PCDA) Langmuir-Blodgett (LB) films reveals a bilayer structure with d-spacing of 4.50 nm [19]. Detailed structural analysis of the LB films investigated by using an in situ grazing incidence X-ray diffraction (GIXRD) is also available [17]. In this study, the XRD pattern of pure poly(PCDA) vesicles prepared in aqueous medium exhibits three diffraction peaks. The bilayer d-spacing calculated



**Fig. 1.** XRD profiles of (a) pure PDA and PDA/ZnO nanocomposites in blue phase, (b) PDA/ZnO nanocomposites in blue and red phases. The red phase was obtained by annealing the PDA/ZnO nanocomposites at 200 °C for 30 min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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