



Controllable thermochromic and phase transition behaviors of polydiacetylene/zinc(II) ion/zinc oxide nanocomposites via photopolymerization: An insight into the molecular level

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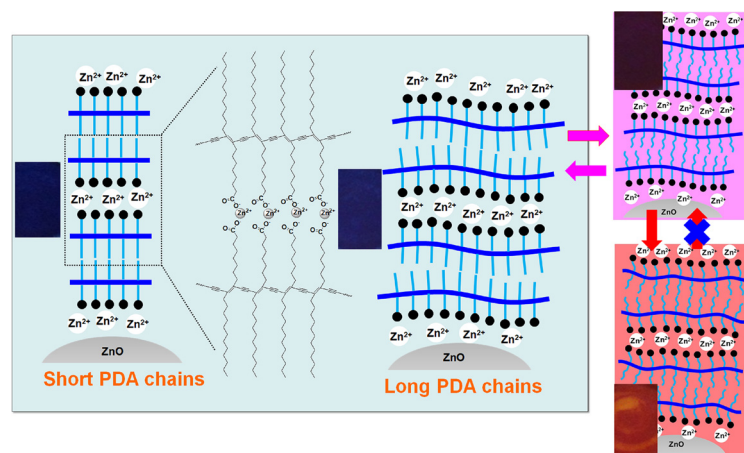
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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Polydiacetylene
Nanocomposite
Thermochromism
Chain length
Phase transition

ABSTRACT

Reversible thermochromic polydiacetylene/zinc(II) ion/zinc oxide (PDA/Zn²⁺/ZnO) nanocomposites with a wide range of color-transition temperature have been prepared by varying photopolymerization time. This contribution presents our continuation study investigating into the molecular origins of this behavior. Infrared spectroscopy is utilized to investigate interfacial interactions of the systems while the conformation of PDA conjugated backbone is probed by Raman spectroscopy. X-ray diffraction explores molecular packing within the nanocomposites. We have found that the increase of photopolymerization time induces the relaxation of PDA backbone into a newly observed state indicated by systematic growth of new vibrational modes of C≡C and C=C bonds. This relaxation process results in the decrease of reversible blue-to-purple color-transition temperature. In contrast, the increase of backbone length with photopolymerization time causes an opposite trend of the irreversible purple-to-red color transition observed at relatively high temperature region. Differential scanning calorimetry detects two distinct phase transitions corresponding to the melting of alkyl side chains and

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<https://doi.org/10.1016/j.colsurfa.2018.06.058>

Received 7 March 2018; Received in revised form 20 June 2018; Accepted 20 June 2018

Available online 21 June 2018

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rigid backbone. These melting temperatures vary with photopolymerization time consistent with the variation of color-transition temperature.

1. Introduction

Polydiacetylenes (PDAs) are known to exhibit a color transition when exposed to various external stimuli such as heat, chemicals, biomolecules, UV light and electricity [1–17]. The color transition, normally from blue to red, occurs rapidly and is easily perceived by naked eyes, rendering PDA-based materials potential candidates for various applications such as 2D and 3D temperature sensors [2], sensors for volatile organic compounds [3,4], sensors for biomolecules [7,10] and a sensor for hydrogen peroxide [15]. The as-prepared PDAs usually present blue phase and are not fluorescent [18]. The blue-to-red color transition of PDAs generally involves segmental rearrangement within PDA assemblies causing the decrease of conjugation length [19–21]. The red-phase PDAs become fluorescent with quantum yield of about 0.02.

Microscopic mechanism of the color transition of PDA has been investigated by utilizing various techniques. Early works on urethane-substituted PDAs illustrated that the color transition was dominated by the change of backbone conformation [22,23]. When the systems were perturbed, the inter- and intrachain interactions were weakened. This allowed segmental rearrangement within the PDA assemblies, affecting the conjugation length of systems. Later works on the PDAs constituting carboxylic head group observed the change of molecular packing during the color-transition process [19–21,24]. Atkinson et al. reported that the color transition of PDA prepared from 10,12-pentacosadiynoic acid (PCDA) was related to the change from the orthorhombic to triclinic structure [24]. Lifshitz et al. observed the decrease of spacing between PDA backbones and the rearrangement of side chains during the color transition [20]. Fujimori et al. also detected the shrinkage of unit cell [21]. Our group utilized nuclear magnetic resonance spectroscopy to follow the molecular dynamics of each segment within PDA chain during the color transition [16]. These previous studies indicate that the segmental rearrangement plays an important role on the mechanism of color transition.

The color-transition properties of PDAs prepared from commercially available monomers such as PCDA are generally irreversible, limiting their utilization in various applications [14,16,25,26]. Many research groups have demonstrated that reversible color transition can be achieved by enhancing the interactions within the PDA assemblies via structural modification [17,27–33] or incorporating foreign materials [1,2,5,14,19,26,34–47]. For example, the PDA functionalized with hydrazide head group exhibits reversible color transition under acid-base treatments [28]. The azobenzene-substituted PDA exhibits

reversible thermochromism due to the enhanced intermolecular π - π interaction [29]. The nanocomposites of PDA/polymers [5,14,26], PDA/cations [1,2,9,34–37] and PDA/metal oxides [38,35–47] can provide reversible thermochromism as well.

Our group has achieved reversible thermochromism of PDAs by incorporating zinc oxide (ZnO) nanoparticles [38–45]. Our latest study revealed the presence of Zn^{2+} ions, releasing from ZnO nanoparticles during the preparation process [44]. These Zn^{2+} ions intercalated between PDA layers and interacted with the carboxylate head groups while the ZnO nanoparticles provided anchoring sites. The PDA/ Zn^{2+} /ZnO nanocomposites possess rather strong inter- and intramolecular interactions, making the system thermochromic reversible [38,39] and highly stable in various organic solvents [42]. The presence of ZnO nanoparticles also allows the colorimetric response to both acids and bases, which extends the utilization as a chemical sensor [40,43,45]. Recently, we have found a simple route for controlling the color-transition temperature of PDA/ Zn^{2+} /ZnO nanocomposites. The increase of photopolymerization time caused systematic variation of the color-transition temperature [41]. In this contribution, we present our continuation work, investigating into the molecular level of the color-transition behaviors of PDA/ Zn^{2+} /ZnO nanocomposites obtained by varying photopolymerization time.

2. Materials and methods

The diacetylene (DA) monomers used in this study, 5,7-hexadecadiynoic acid (HDDA), 10,12-tricosadiynoic acid (TCDA) and 10,12-pentacosadiynoic acid (PCDA) were commercially available at Fluka. The ZnO nanoparticles were purchased from Nano Materials Technology (Thailand). The diameter of ZnO nanoparticles revealed by transmission electron microscopy (TEM, Tecnai 12, D291) is ranged from 20 to 160 nm (Fig. 1a) with the averaged diameter of 65 nm. The PDA/ Zn^{2+} /ZnO nanocomposites were prepared using a method described in our previous study [41]. Briefly, the DA monomer and ZnO nanoparticles were co-dispersed in water assisted by an ultrasonication. The concentration of DA monomer was 0.5 mM while the ZnO/DA ratio was 10 wt%. The DA/ZnO aqueous suspension was incubated at $\sim 4^\circ\text{C}$ for ~ 24 h, followed by UV light irradiation ($\lambda \sim 254$ nm, 10 W). The photopolymerization time was increased from 5 to 120 min, yielding a blue suspension of PDA/ Zn^{2+} /ZnO nanocomposite. The suspension was filtered through 1.2 μm pore size cellulose acetate membrane. Thin films were prepared by drop-casting the nanocomposite suspension onto glass slides and drying in a vacuum oven overnight. Particle size of

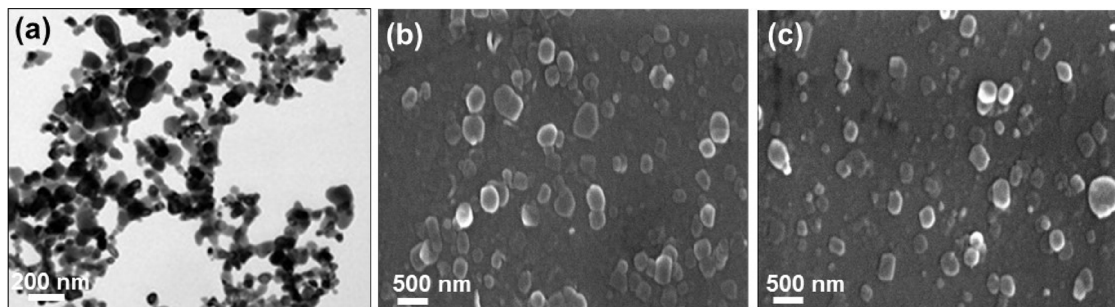


Fig. 1. (a) TEM image of ZnO nanoparticles. SEM images of (b) poly(PCDA)/ Zn^{2+} /ZnO5m and poly(PCDA)/ Zn^{2+} /ZnO60m prepared by using photopolymerization time of 5 and 60 min, respectively.

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