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High color stability and reversible thermochromism of polydiacetylene/zinc oxide nanocomposite in various organic solvents and polymer matrices

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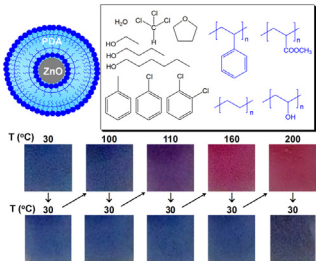
HIGHLIGHTS

- Polydiacetylene/zinc oxide (PDA/ZnO) nanocomposites are dispersed in various organic solvents.
- PDA/ZnO nanocomposites remain blue and still exhibit reversible thermochromism.
- PDA/ZnO nanocomposites can be embedded in poly(styrene), poly(methyl methacrylate), poly(ethylene) and poly(vinyl alcohol) films.
- Complete color reversibility of some systems persists up to 200 °C.
- Our result can largely extend the utilization of PDA-based materials.

GRAPHICAL ABSTRACT



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ABSTRACT

Polydiacetylene (PDA)-based materials exhibit color transition when subjected to external stimuli, making them attractive for sensing technology. The utilization of PDA-based materials can be largely extended by fabricating in different polymer matrices, which normally involves organic solvents as media. Recently, our group has developed PDA/zinc oxide (ZnO) nanocomposites, exhibiting reversible thermochromism in aqueous medium. In this contribution, we demonstrate that the PDA/ZnO nanocomposite can be dispersed in various organic solvents including 1,2-dichlorobenzene, chlorobenzene, toluene, ethanol, butanol, hexanol, chloroform and tetrahydrofuran. The color of pure PDA changes from blue to red in these solvents while the PDA/ZnO nanocomposite remains blue after 30 days. The color reversibility and color-transition temperature of the PDA/ZnO nanocomposite are hardly affected in these organic solvents compared to the system of aqueous medium. We further demonstrate that the PDA/ZnO nanocomposite can be embedded in common polymer matrices such as poly(styrene), poly(methyl methacrylate), poly(ethylene) and poly(vinyl alcohol) by using a simple mixing process. We have found that color reversibility of the PDA/ZnO nanocomposite depends on property of the polymer matrices and persists up to about 200 °C in some systems. The ability to prepare PDA-based materials in different organic solvents and polymer matrices is very important for their utilization in various applications.

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1. Introduction

Polydiacetylene (PDA) is one of the conjugated polymers that exhibit colorimetric response to external stimuli. Utilizing this class of material for sensing technology has received much attention from scientific community over the past few decades [1–10]. Under suitable conditions, diacetylene (DA) monomers constituting polar head and alkyl tail can assemble into vesicular structure in aqueous medium [4,5,11–13]. Topopolymerization by UV light irradiation results in PDA vesicles with ordered side chain arrangement and ene-yne conjugated backbone. Common PDAs exhibit a blue-to-red color transition when subjected to some chemicals [12–23], temperature [4–11,24–35], acids and bases [13,36–42], ions [43–46] and pressure [47]. The perturbation induces segmental rearrangement within the PDA assemblies, altering the electronic states and hence optical absorption spectrum [6,7,25,48–50].

Controlling color-transition temperature and reversible/irreversible thermochromic behaviors by chemical modifications of PDA structure is effective [4,5,9,10,13,26,27,51], however, expensive and time-consuming. Recently, we introduce a relatively simple and cheap method for controlling the color-transition behaviors of PDAs [32,33,39]. By incorporating zinc oxide (ZnO) nanoparticles into the PDA assemblies, strong interfacial interactions significantly change the color-transition behavior. The PDA/ZnO nanocomposite exhibits higher color transition temperature than the pure PDAs, and, furthermore, reversible thermochromism. The following works by other groups observe similar results [34,35]. Our following works show that the color-transition temperature of the nanocomposite can be systematically tuned by varying the alkyl chain length of PDA and the photopolymerization time [33,52].

To extend their utilization in applications, PDAs are immobilized into solid state matrices. Various fabrication methods including electrospinning into fibers [53–55], fabricating into microtubes [56] and helical chain [57], multilayer depositing onto substrates [58,59], entrapping in sol–gel matrix [60–62] and drop casting or printing on paper [63,64] are employed. Each technique improves versatility, stability and mechanical strength of PDAs. However, the disadvantages include complicate material and equipment parameters, long response time and reduced sensitivity.

One of the most straightforward methods is fabricating PDAs films by mixing with polymer matrices and then casting in Petri dish or spin casting [18,65]. Film thickness can be easily controlled and a homogeneous, flexible film can be obtained. A simple mixing-drying process was carried out by Kim et al. to embed PDAs in polyvinyl alcohol (PVA) matrix [65]. Film casting was carried out in a Petri dish and dried at room temperature. The PDA embedded in PVA film typically changes from blue to red at elevated temperature. This approach is simple; however, only water-soluble polymers can be used as matrices. This is because the common PDAs with carboxylic head group exhibit colorimetric response to organic solvents such as chloroform, THF, ethyl acetate, alkanes and alcohols [12,13,17,18,23,66]. Perturbation mechanism involves the swelling of PDA by penetration of solvent molecules, which breaks hydrogen bonds between the head groups and weakens the dispersion interactions [12,13,66]. The segmental rearrangement leads to the blue-to-red color transition. PDA/ZnO nanocomposite, on the other hand, shows high color stability due to the presence of strong interfacial interactions [32]. Thus, utilization of organic solvents as media for this class of material is promising.

In this continuing research, we investigate the color stability of PDA/ZnO nanocomposite in various organic solvents including 1,2-dichlorobenzene, chlorobenzene, toluene, ethanol, butanol, hexanol, chloroform and tetrahydrofuran. Morphology, particle size distribution and optical properties of the PDA/ZnO nanocomposite dispersed in these organic solvents are examined. We also demonstrates that the PDA/ZnO nanocomposite can be embedded in common polymer matrices including polystyrene (PS), poly(methyl methacrylate) (PMMA), polyethylene (PE) and polyvinyl alcohol (PVA). These nanocomposite films exhibit reversible thermochromism in relatively wide range of temperature. Our research is important for extending the utilization of PDA-based materials in various applications.

Table 1
Physical properties of solvents [67].

Solvents	Properties		
	Boiling point (°C)	Dielectric constant (20 °C)	Electric dipole moment in Debye units
1,2-Dichlorobenzene	180.0	9.93 (25 °C)	2.50
Chlorobenzene	131.70	2.708	1.69
Toluene	110.60	2.379 (25 °C)	0.37
Ethanol	78.29	25.30	1.69
1-Butanol	117.70	17.80	1.66
1-Hexanol	157.55	13.03	–
Water	100.00	80.10	1.85
THF	64.80	7.600	1.75
Chloroform	61.20	4.81	1.01

2. Experimental

Monomer used in this study, 10,12-pentacosadiynoic acid (PCDA), was commercially available at Fluka. ZnO nanoparticles with diameter in the range of 20–200 nm were purchased from Nano Materials Technology, Thailand. All of the organic solvents (AR grade) were obtained from RCI Labscan Limited, Thailand. The preparation procedure of poly(PCDA)/ZnO nanocomposite was slightly modified from our previous report [32]. The PCDA monomer is dissolved in ethanol and then filtered using 0.45 μm pore size nylon membrane to remove polymerized materials. The PCDA solution was slowly injected into ZnO aqueous suspension, which was under ultrasonication. The suspension was continuously stirred at 80 °C for about 30 min to remove the ethanol. The final concentration of PCDA in the suspension was 0.5 mM and the ZnO/PCDA ratio was 10 wt.%. The suspension was cooled down to room temperature and then kept at ~4 °C for ~24 h to allow the self-assembling of PCDA monomer onto ZnO nanoparticles. The poly(PCDA)/ZnO nanocomposite with deep blue color was obtained by UV light irradiation (λ ~ 254 nm, 10 W) for 5 min. The aqueous suspension was divided into small portions and then dried at 45 °C for 48 h. The characterization of poly(PCDA)/ZnO nancomposite by using various techniques is available in previous studies (see supporting information) [32–35].

Organic solvents used in this study are categorized into aromatic solvents, alcohols and other common solvents. Structure and polarity of solvents are systematically varied (see Table 1), which could results in the variation of local interactions with the poly(PCDA) segments. To disperse the poly(PCDA)/ZnO nanocomposite in solvents, 1,2-dichlorobenzene, chlorobenzene, toluene, ethanol, butanol, hexanol, chloroform, tetrahydrofuran (THF) and deionized water were added to the dried samples. Then, suspensions were ultrasonicated for 10 min. The final concentration of these suspensions is 0.5 mM. All samples in this study were not filtered, providing higher concentration of poly(PCDA)/ZnO nanocomposite and larger particle size distribution compared to our previous reports [32,33].

Size distribution of the poly(PCDA)/ZnO nanocomposite dispersed in various solvents was investigated by dynamic light scattering (DLS) technique (Brookhaven, ZetaPaLs). The