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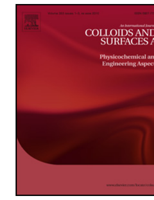

Fine tuning the colorimetric response to thermal and chemical stimuli of polydiacetylene vesicles by using various alcohols as additives

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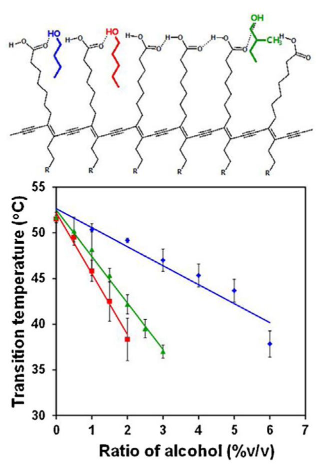
HIGHLIGHTS

- A simple approach for fine tuning colorimetric response of polydiacetylene (PDA) is introduced.
- Addition of alcohols weakens the interactions within PDA assemblies.
- The irreversible color-transition temperature of PDAs can be tuned between 35 and 55 °C.
- Sensitivity of PDAs to chemical stimuli can also be controlled by using alcohols as additives.
- Our approach is simple and systematic, extending their utilization in various applications.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we demonstrate a simple approach for fine tuning the color-transition behaviors of polydiacetylene (PDA) vesicles when exposed to thermal or chemical stimuli. The strength of inter- and intrachain interactions within PDA vesicles, fabricated by using 10,12-tricosadiynoic acid (TCDA) and 10,12-pentacosadiynoic acid (PCDA), are manipulated by mixing with 1-butanol, 1-pentanol or 2-methyl-1-butanol. The swelling of alcohol molecules weakens the interactions within the PDA layers, which in turn affects the color-transition behaviors. We observe that the resultant PDA vesicles exhibit color-transition temperatures ranging from about 35 °C to 55 °C, depending on concentration and structure of the added alcohols. The color-transition temperature and alcohol concentration exhibits linear correlation, where its slope varies with the alcohol structure. This approach is further utilized for controlling the color-transition behaviors of these PDA vesicles upon exposure to chemical stimuli including

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tetrahydrofuran, pyridine, ethylamine and phenol. The color transition of PDA vesicles at desired concentration of each chemical stimulus can be achieved by varying the concentration of alcohol additives. The ability to control the color-transition behaviors of PDA vesicles is very important for their development as chromatic sensor, extending their utilization in various applications.

1. Introduction

Polydiacetylene (PDA) is an ene-yne π-conjugated polymer which can be prepared by UV or γ-irradiation of self-assembled diacetylene (DA) supramolecules [1,2]. One of the most interesting properties of PDAs is their chromatic property. It has been known that PDA assemblies can undergo a color transition, typically changing from blue to red, upon exposure to various external stimuli such as heat [1–16], chemicals [17–25], acids or bases [26–32], ions [33–37] and biomolecules [38–41]. The perturbation of PDA assemblies by external stimuli causes segmental rearrangement, which in turn results in the widening of HOMO-LUMO energy gap and hence the color transition [2,15,42–45]. The chromatic property of PDAs is very attractive for various sensing applications [41,46–48].

To realize the full potential of PDA-based materials, an ability to control the color-transition behaviors is essential. The strength of inter- and intrachain interactions within the PDA assemblies is a key parameter, dictating their color transition. Scientific community has made tremendous efforts, seeking systematic method to control the color-transition behaviors of PDAs. The modification of head group and/or side chain is one of the most effective approach that provides series of PDAs with various color-transition temperatures [3–7,12,14,21]. For example, an increase of alkyl side chain length enhances the dispersion interactions within PDA assemblies, which results in the increase of color-transition temperature [4,21]. In some systems where the head groups constitute aromatic moieties, the PDAs exhibit reversible thermochromism due to the presence of strong hydrogen bond and π–π interactions [14]. Recent study by Wacharsindhu et al. also shows that the bonding of two head groups with alkyl spacer also leads to reversible thermochromism [12]. However, these studies also realize that it is rather difficult to fine tuning the color-transition temperature of PDAs. In addition, the synthetic routes normally involve complicated multi-step methods and time-consuming purification processes.

The incorporation of foreign materials into PDA assemblies is an alternative approach that can provide systematic control over their properties. Various types of additives have been used. For example, the intercalation of Zn^{2+} ion [44] or Na^{+} ion [15,49] with carboxylate head groups of PDAs leads to reversible thermochromism. Similar results are obtained when poly(vinylpyrrolidone) [50] or poly(vinylalcohol) [51] is used. Recent studies by one of the authors also show that reversible thermochromism of the PDAs can be achieved by simply adding zinc oxide (ZnO) nanoparticles into the system [8–11]. Furthermore, color-transition temperature of the thermoreversible PDA/ZnO nanocomposites can be systematically varied between 40 °C and 85 °C by changing photopolymerization time [9] or the length of PDA alkyl side chain [10].

The use of additives for manipulating the irreversible color-transition temperature of PDAs is rarely investigated. Recent study by Gou et al. shows that the addition of triblock copolymers, poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol), into aqueous suspension of PDA vesicles leads to systematic decrease of their color-transition temperature [13]. In addition, at fixed temperature, the PDA vesicles change their color upon increasing the incubation time. According to the authors, these PDA vesicle sensors can be applied for the detection of time-temperature history of bio-products such as vaccines, bio-drugs during the transportation and/or storage. However, the use of this system as irreversible thermosensor is not applicable because the polymeric additives induce relatively fast color transition.

In this study, we seek new additives that can finely tune the color-transition behaviors of PDA vesicles while the color stability is still high. Previous studies of our group show that the molecules of alcohols can penetrate into the layer of PDA vesicle, which in turn weakens inter- and intrachain interactions within the system [20,21]. This perturbation leads to color transition from blue to red at relatively high alcohol concentration. However, the blue color of PDAs is quite stable when a small amount of alcohols is added. Here, we demonstrate the potential of alcohols as additives for fine tuning the color-transition behaviors of PDA vesicles, fabricated from 10,12-tricosadiynoic acid (TCDA) and 10,12-pentacosadiynoic acid (PCDA). Three types of alcohols including 1-butanol, 1-pentanol and 2-methyl-1-butanol are investigated. Our results show that the color-transition behaviors of these PDAs upon exposure to thermal or various chemical stimuli depends on structure and concentration of the added alcohols.

2. Materials and method

The TCDA, PCDA monomers (Fluka) and other chemicals (AR grade, Aldrich) were commercially available. Their physical properties are shown in Table 1. The pure PDA vesicles in aqueous media were prepared as described in our previous reports [20,21]. The alcohols were added into PDA aqueous suspensions at various concentrations by using micropipette. All PDA suspensions were kept at room temperature and away from light for a week. The stability of these poly(TCDA) and poly(PCDA) suspensions were followed by measuring the absorption spectra and taking their photographs. The absorption spectra were measured by using UV–vis spectrometer (Analytik Jena Specord S100) equipped with diode array detector and variable-temperature sample holder. The concentration of PDA suspension in each experiment was controlled to be the same by adjusting the absorbance value. The size of PDA vesicles was measured by using dynamic light scattering (Marvern Instruments Zetasizer nanoseries Nano-ZS). The morphologies of PDA vesicles were studied by using scanning electron microscope (SEM, LEO 1455 VP). The samples were prepared by dropping the vesicle suspension on a polished silicon substrate.

After the addition of alcohols, the poly(TCDA) and poly(PCDA) suspensions were kept at room temperature and away from light

Table 1
Physical properties of chemicals used in this study [52].

Chemicals	Dielectric constant	Solubility in water (g/L) at 25 °C
1-Propanol	20.80	Miscible
1-Butanol	17.84	80.0
1-Pentanol	15.13	22.4
2-Methyl-1-butanol	15.63	31.0
Tetrahydrofuran	7.52	Miscible
Pyridine	12.40	Miscible
Ethylamine	6.3	Miscible
Phenol	9.9	8.3