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Versatile route to prepare reversible thermochromic polydiacetylene nanocomposite using low molecular weight poly(vinylpyrrolidone)

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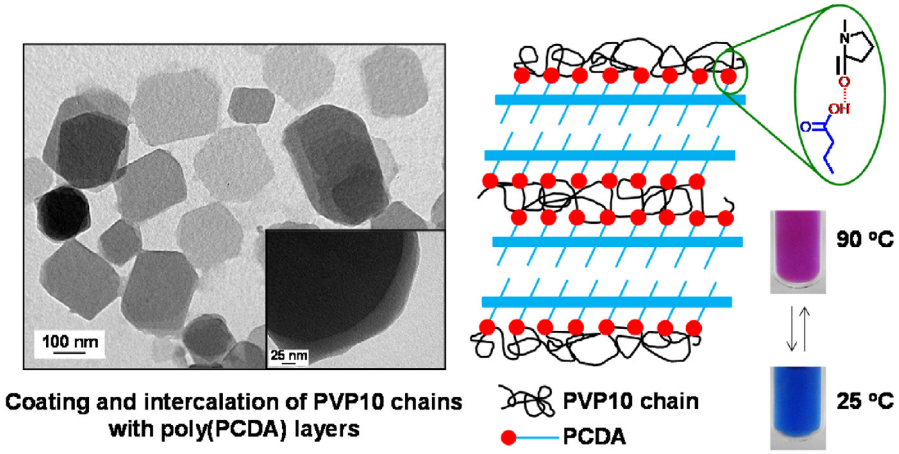
HIGHLIGHTS

- Reversible thermochromic polydiacetylene(PDA) nanocomposite is simply prepared.
- Intercalation of short poly(vinylpyrrolidone)(PVP10) chains and PDA layers takes place in aqueous medium.
- Reversible blue-to-purple color transition occurs at 90 °C in aqueous suspension.
- Reversible thermochromism of thin film persists up to 200 °C.
- Our simple methods can extend the utilization of PDA in many applications.

GRAPHICAL ABSTRACT



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ABSTRACT

This contribution introduces a simple method to prepare polydiacetylene(PDA)-based materials with reversible thermochromism. The incorporation of low molecular weight poly(vinylpyrrolidone) (PVP10) into the PDA assemblies, prepared from 10,12-pentacosadiynoic acid (PCDA) monomer, enhances inter- and intrachain interactions within the system. The PVP10 is simply added during conventional preparation methods without requiring any other treatments. X-ray diffraction technique reveals the increase of interlamellar distance, which indicates the intercalation of PVP10 chains with the poly(PCDA) layers. The resultant poly(PCDA)/PVP10 nanocomposite exhibits higher color-transition temperature compared to that of the pure poly(PCDA) assemblies. In addition, the blue-to-purple color transition of poly(PCDA)/PVP10 nanocomposite in aqueous solution is fully reversible during 10 consecutive heating/cooling cycles. When the poly(PCDA)/PVP10 nanocomposite is fabricated into thin film, it exhibits two-steps color transition, reversible blue-to-purple at 90 °C and reversible purple-to-red at 150 °C. The complete color reversibility of this system persists up to 200 °C. Raman scattering spectroscopy is utilized to investigate color stability and the change of PDA backbone conformation within the nanocomposite

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during the color-transition process. We also demonstrate that the preparation conditions such as the PVP10 concentration and incubation time significantly affect the color reversibility of the resultant nanocomposites. Their size and shape are influenced by the PCDA/PVP10 mixing process.

1. Introduction

Polydiacetylene(PDA) assemblies are known to undergo a color transition upon exposure to heat [1–10], chemicals [11–16], acids or bases [17–22], ions [23–27] and biomolecules [28–32]. This unique property leads to their potential utilization in various sensing applications. One of the most studied PDA, prepared from the commercially available 10,12-pentacosadiynoic acid (PCDA), exhibits irreversible blue-to-red color transition at ~55 °C [4,5,17]. To extend their applications, an ability to tune color-transition temperature as well as color reversibility is very important. Structural modification can provide different classes of PDAs with various thermochromic properties. The differences of functional head group [2,3,8–10,17], alkyl tail length [17,33], diacetylene position [34], number of head groups and linkers [9,35–37] of PDAs cause the variation of color-transition temperature. The increase of inter- and intrachain interactions within PDA assemblies generally elevates the color-transition temperature and, in some cases, provides reversible thermochromism [8–10,37]. However, the synthetic routes of new diacetylene (DA) monomers normally involve complicated processes, require expensive reagents and sometime provide unexpected results [33,37]. Therefore, it is very important to seek alternative approaches for controlling the thermochromic properties of PDAs.

The incorporation of foreign materials into PDA assemblies is also a very effective method for manipulating the color-transition behaviors of PDAs. Recent study by Lee et al. illustrates that the addition of Cs^+ ion into poly(PCDA) assemblies results in reversible thermochromism [38]. Furthermore, thin film of the poly(PCDA)-Cs assemblies exhibits color transition upon exposure to water, which in turn extends their utilization in other applications. The use of other cations including Li^+ [39], Na^+ [40,41], Zn^{2+}[42] and Dy^{3+}[43] also yield reversible thermochromism. In these systems, the cations strongly interact with negatively charged carboxylate head groups of the poly(PCDA), significantly enhancing inter- and intrachain interactions within the assemblies. Our group recently introduces a new type of material, ZnO nanoparticles, for controlling the color-transition behaviors of PDAs [44–49]. The PDA/ZnO nanocomposites exhibit reversible thermochromism and, interestingly, response to both acid and base [46,49]. The color-transition temperature of this system can be tuned by simply varying the photopolymerization time [48].

Polymeric materials have been utilized for the development of PDA systems, playing roles as both additive and matrix for thin film preparation. Highly stable PDA films for sensing various chemicals can be prepared by mixing with poly(4-vinylpyridine) (P4VP). Strong hydrogen bonding between PDA domains and P4VP chains resists the dissolution of the film in many organic solvents [50]. Gou et al. [51] and Lu et al. [52] have shown that the addition of poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol) and poly(N-isopropylacrylamide), respectively, at various concentrations induces systematic decrease of the color-transition temperature of PDAs. The use of long chain alcohols as additives provides similar results [4]. These PDA/polymer assemblies still exhibit irreversible thermochromism. Study by Gu et al. demonstrates that reversible thermochromism of PDA can be achieved by using relatively high molecular weight (MW) poly(vinylpyrrolidone) (PVP) (MW = 280,000 g/mol) [53]. According to their small angle X-ray scattering data, the authors propose that PVP chains penetrate into the PDA layers, forming hydrogen bonds with the carboxylic head groups. To obtain this architecture, the samples have to be prepared into thin films and thermally annealed just above the PDA melting point for an extended period of time. Although the color reversibility of PDA/PVP nanocomposite can extends their utilization in many applications, the complicated process becomes problematic for large scale production.

In this contribution, we introduce low MW PVP10, (MW = 10,000 g/mol), as an additive for preparing PDA-based materials with reversible thermochromism. The relatively short PVP10 chains are expected to facilitate the penetration into PDA layers. In fact, we can achieve reversible thermochromism of PDA assemblies in aqueous medium and thin film by using conventional preparation methods without requiring any additional treatment. Our approach is quite simple and uses the commercially available PDA and PVP polymers. This is very important for large scale utilization.

2. Materials and method

PCDA monomers and PVP10 (MW = 10,000 g/mol) were purchased from Aldrich. The poly(PCDA) vesicles and poly(PCDA)/PVP10 nanocomposites were prepared by using conventional route, namely the dry method. PCDA monomers were dissolved in ethanol at 1.25 mg/ml and then filtered by using 0.45 μm nylon filter to remove residual polymer. The PCDA solution was slowly dried at 60 °C in water bath. The PVP10 aqueous solution was added into the PCDA film to provide the concentration of 0.25 mM. The concentration of PVP10 aqueous solution was varied from 0 to 5 mg/ml. The samples were sonicated at 80 °C for 90 min to disperse the PCDA monomers into aqueous medium. The PCDA/PVP10 solutions were allowed to equilibrate at room temperature and then stored at 4 °C overnight to induce the self-assembling process. Topopolymerization of the PCDA/PVP10 assemblies was carried out by illuminating with UV light (10 W, λ ~ 254 nm) for 5 min, resulting in a blue suspension.

Thermochromic property of pure poly(PCDA) assemblies and poly(PCDA)/PVP10 nanocomposites in aqueous solution was studied by using UV/vis absorption spectrophotometer (Analytik Jena Specord 210 Plus) equipped with peltier temperature controller. The colorimetric response (%CR) of pure poly(PCDA) was calculated as follows: $\%CR = [(PB_0 - PB)/PB_0] \times 100$. The PB is the percent blue calculated from $A_{640}/(A_{540} + A_{640})$, where A_{540} and A_{640} are the absorbance of red (λ = 540) and blue (λ = 640) phases of poly(PCDA), respectively. The initial PB_0 value was determined at room temperature. Since the color of poly(PCDA)/PVP10 nanocomposites changes to purple at elevated temperature, the A_{540} is replaced by A_{580}. The poly(PCDA)/PVP10 nanocomposite was fabricated into thin film by drop casting onto a glass slide, followed by air-drying at room temperature. Color transition of the nanocomposite film was studied by heating from 30 to 200 °C using 10 °C interval. The film was equilibrated at each temperature for 2 min prior to each measurement. The film was periodically cooled to room temperature to investigate the color reversibility.