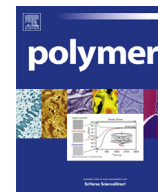




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Reversible thermochromism via hydrogen-bonded cocrystals of polydiacetylene and melamine

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ABSTRACT

In this study, we report a unique two-step approach to prepare pure and well-organized 10,12-pentacosadiynoic acid (DA)/melamine (MA) cocrystals, from which the topochemically polymerized product, poly(10,12-pentacosadiynoic acid) (PDA)/MA cocrystals, demonstrated reversible thermochromism (note that PDA in its pure crystalline form is thermochromically irreversible). In the first step, co-assembling DA and MA was achieved in a selective solvent for MA (i.e., water) using the non-covalently connected micelle method. In the second step, annealing the DA/MA co-assembly at a temperature higher than the melting point of pure DA crystals (62 °C) but below that of the cocrystals (87 °C) led to the formation of pure DA/MA cocrystals with a molar ratio of 2:1. The resultant lath-like DA/MA cocrystals were nano-sized and had an alternating DA/MA lamellar structure. Due to the strong intermolecular hydrogen-bonding and π - π stacking of MA molecules, the topochemically polymerized PDA/MA cocrystals were completely reversible in thermochromism. This is the first example that reversible thermochromism of PDA is realized through hydrogen-bonding assisted cocrystals with a small molecule.

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1. Introduction

Polydiacetylenes, which are products of topochemical polymerization of properly packed (or crystallized) diacetylene monomers [1,2], are promising for chemical and biological sensors because of their color and fluorescent responses to environmental stimuli [3,4], such as heat [5–8], pH [9,10], solvents [11,12], ions [13–15], interactions with biological species [16–18], stresses [19,20], and electrical or magnetic field [21,22]. However, the color and fluorescent changes of polydiacetylenes are usually irreversible, which prevent them from being reusable. Therefore, it is highly desirable to achieve reversible thermochromism for polydiacetylenes using facile ways. Generally speaking, reversible thermochromism of polydiacetylenes requires simultaneous

control of the self-assembled structure of the precursor diacetylene molecules and interactions within the system [23–27]. Specifically, each side chain of polydiacetylenes should be tethered to a solid substrate, and the tethering should not introduce defects into the crystal structure of the side chains [28–30]. For complete reversibility, pure polydiacetylene crystals have to be removed from the system since they are irreversible in nature. In previous studies, we have reported that complete thermochromic reversibility of poly(10,12-pentacosadiynoic acid) (PDA), which in its pure crystalline form is irreversible, could be successfully achieved in polymer blends with a properly intercalated “brick-and-mortar” structure [23,26]. In this brick-and-mortar nanostructure, nearly all the side chains in the PDA are tethered via hydrogen bonding (H-bonding) to the polymer matrix. Ideally, pure cocrystals of polydiacetylenes and the other component, which can form a solid substrate for tethering the DA side chains, should be more desirable for complete thermochromic reversibility. However, no such cocrystals of polydiacetylenes have been reported so far [31–33].

Cocrystallization is a powerful approach to combine multiple

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functionalities of two or more components together for solid state chemistry, pharmaceutical science and semiconductor industry [34–36]. The components in a cocrystal are mixed at the molecular level and arranged in the same crystalline lattice. This is beneficial for cooperative effects among different components, and could lead to new property or functionality that is not present in each component alone [35,37,38]. In some cases, pure cocrystals are required for maximizing their cooperation [36]. From literature reports, cocrystals have been prepared by cocrystallization during co-precipitation in solution, cocrystallization in the melt, or cocrystallization by grinding. In these cases, pure cocrystals can only be prepared when the interactions between different components are strong enough to overcome the tendency of phase separation and self-crystallization [39,40]. Also, the melt crystallization and grinding methods cannot be applied when any of the components is thermally or mechanically sensitive [41].

In this study, we report that melamine (MA) can form cocrystals with 10,12-pentacosadiynoic acid (DA), a commercially available diacetylene monomer. Although MA has a strong tendency to self-crystallization and the interaction between DA and MA is relatively weak, phase separation between the two components and self-crystallization of MA are successfully prevented by carrying out the co-assembly and cocrystallization in a selective solvent of MA, i.e., water. Especially, by annealing the DA/MA co-assembly above the melting temperature (T_m) of DA crystals ($\sim 62^\circ\text{C}$) but below the T_m (87°C) of the cocrystals, pure and well-organized DA/MA cocrystals with a molar ratio of 2:1 are achieved as a result of intermolecular H-bonding. The resultant lath-like DA/MA cocrystals are nano-sized and have an alternating DA/MA lamellar structure. After topological polymerization, the resultant poly(10,12-pentacosadiynoic acid) (PDA)/MA cocrystals are completely reversible in thermochromism (see Fig. 1). It is the first example to achieve complete reversibility through DA cocrystals with another small molecule, and this will open a new avenue for developing completely reversible polydiacetylenes.

2. Experimental

2.1. Materials

10,12-pentacosadiynoic acid (DA), $\text{CH}_3(\text{CH}_2)_{11}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(-\text{CH}_2)_8-\text{COOH}$, was purchased from GFS Chemicals, Inc. Melamine (Chemical Reagent grade) and absolute ethanol were purchased from Sinopham Chemical Reagent Co., Ltd, China. All reagents and solvents were used as received without further purification.

2.2. Preparation of DA/MA cocrystals via the NCCM method

DA was dissolved in absolute ethanol at a concentration of 1.25 mg/mL. The solution was filtered through a $0.45\ \mu\text{m}$ filter to remove any polymerized PDA impurity ($<5\ \text{wt}\%$) before use. MA was dissolved in water at a concentration of 3.0 mg/mL. DA/MA co-assembly was prepared by adding 16 mL of DA/ethanol solution into 200 mL of MA aqueous solution under rigorous stirring at ambient temperature. Quickly, the mixed solution became translucent, and the glass vials containing suspension of the DA/MA co-assemblies was sealed, followed by annealing at 25, 50, and 65°C , respectively, for 6 h in a gravity convection oven. The respective suspensions were stringently dialyzed against deionized water for a week to completely remove free MA.

2.3. Preparation of PDA/MA suspension and powders

The DA/MA powder was separated by centrifugation at 12,000 revolutions/min (rpm) for more than 1 h. After collection, the powder was further dried in a freeze-drier for one week. Elemental analysis (EA) of the DA/MA powder was carried out using a Vario EL III elemental analyzer. The EA result showed that the DA/MA molar ratio was 2:1: Anal. Calculated for $\text{C}_{53}\text{H}_{90}\text{N}_6\text{O}_4$ (i.e., $2\text{C}_{25}\text{H}_{42}\text{O}_2:\text{C}_3\text{H}_6\text{N}_6$): C, 72.72%; H, 10.36%; N, 9.60%; Found: C, 72.93%; H, 10.19%; N, 9.42%. The PDA/MA suspensions were prepared by exposure to a UV light with a wavelength of 254 nm for 10 min. PDA/MA powders were obtained by using the same process as that for DA/MA powders, except for the step of UV exposure with a shorter time (30 s).

2.4. Characterization methods

Differential scanning calorimetry (DSC) was carried out using a TA Instruments differential scanning calorimeter. All experiments were carried out under a nitrogen atmosphere by heating/cooling at a rate of $10^\circ\text{C}/\text{min}$. Fourier transform infrared (FTIR) spectra were recorded using a Nicolet Nexus 470 infrared spectrometer at a resolution of $4\ \text{cm}^{-1}$, and 64 scans were used for an acceptable signal-to-noise ratio. Thermochromic UV–Vis absorption spectra were obtained on a Spectrophotometer Lambda 35 (Perkin Elmer, Inc.). The highest temperature for the measurement was 90°C due to the instrument limitation.

One-dimensional (1D) powder X-ray diffraction (XRD) was conducted on a PANalytical X'Pert PRO diffractometer, operating at 40 kV and 40 mA with Cu $K\alpha$ radiation at wavelength

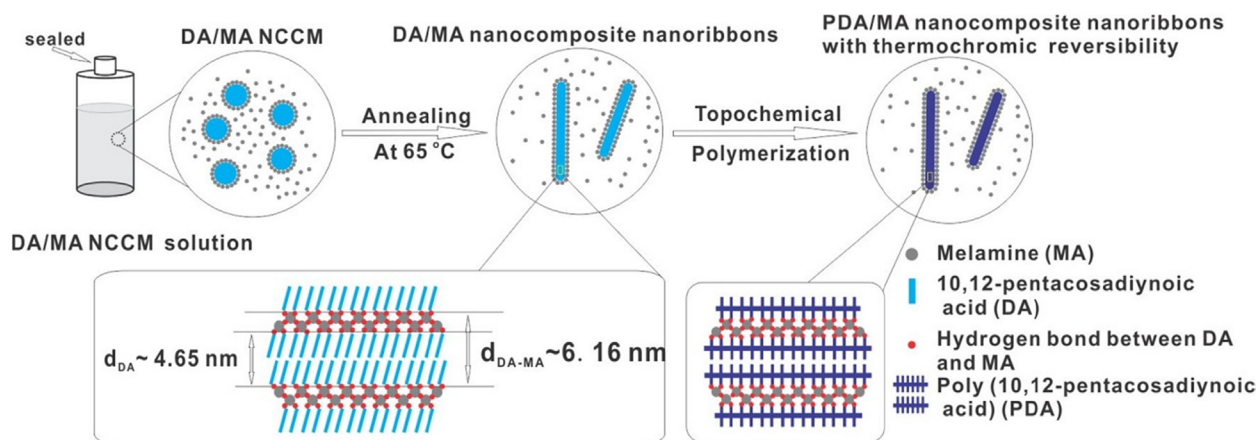


Fig. 1. Schematic illustration of the preparation process for reversibly thermochromic PDA/MA cocrystals. NCCM is non-covalently connected micelle.

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