

A novel approach to polydiacetylenic nanomaterials with thermochromatic reversibility

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Abstract Two organic building molecules, 5, 7-octadecadiynoic acid (OCDA) and p-xyxylenediamine, complex in THF solutions and assemble into thin films with a highly ordered lamellar structure after evaporation of the solvent. Topochemical polymerization of diacetylene components in OCDA produces polydiacetylenic nanocomposites, which show reversible chromatic transition between blue and red under thermal stimuli. In addition, the nanomaterials also exhibit a blue-to-red color change once exposed to various solvents. These properties endow them with potential applications as optoelectronic and sensing devices.

Introduction

The extensive networks of hydrogen bonding, π - π stacking, hydrophobic, and electrostatic interactions in supramolecular assemblies, has resulted in materials with tunable molecular alignment and novel functionality [1–5]. Essentially, small molecular building blocks self-assemble into highly ordered and interconnected configurations, based on molecular sizes and tunable intra-molecular forces [6]. For example, supramolecular materials such as muconates [7], amphiphilic diacetylenes [8], and polymeric supramolecules [9] have precise molecular organization,

and tunable properties that may eventually be useful for self-healing materials, molecular sensors, heterogeneous catalysts, separation devices, and nonlinear optics. The same interactions among building blocks also allow self-assembly into materials that reversibly respond to external, thermal, or chemical stimuli by structural rearrangement. Examples of these materials include polymeric amino acids with thermal responsiveness [10], or primary ammonium carboxylate poly (muconic acid) with pH and amine sensing functionality [7].

The conformation control and tunable properties afforded by this new class of supramolecular materials would be particularly useful for functional materials containing conjugated polymers. These conjugated polymers can act as visible, fluorescent, or electric indicators, that reversibly respond to stimuli-induced structural rearrangement. Owing to extended π electron delocalization along their backbones, conjugated organic polymers exhibit optical properties for applications ranging from optical devices to chemical sensors [11]. Furthermore, incorporating conjugated polymers such as poly (phenylenevinylene) [12], polyaniline [13], polythiophene, polypyrrole, polyacetylene [14], and polydiacetylene [15] into ordered nanocomposites aligns chains, enhances fluorescence [12], protects from environmental degradation [14], and controls interchain energy transfer [16].

Blue-colored polydiacetylene is of particular interest, because, the optical absorption blue-shifts dramatically when thermal, mechanical, or chemical stress is applied to the backbone through pendant side chains. This structure-induced response has been explored as a colorimetric transduction scheme in a variety of chemical and physical sensor designs [17]. Polydiacetylene research has resulted in vesicles [18], crystals [19], solids [20], solutions [21], cast films [22], Langmuir films [23], Langmuir-Blodgett

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films [24], chemical sensors [8], polydiacetylene/polyallylamine monolayers [25], and three-dimensional silica/PDA nanocomposites [26, 27]. However, synthesis of PDA materials with truly reversible color is still challenging, and it is available only by careful control of the polymer chain alignment [28–30]. Recently, Peng et al. reported two successful PDA systems with really repeatable and reversible color changes based on the introduction of a rigid inorganic network [29, 30]. Since the PDA color change is attributed to the effective conjugation length variety of delocalized, π -conjugated polymer backbones under external stimuli, the robust inorganic framework in Peng's systems will help the reversible transition of PDA backbone conformations. These PDA materials with real chromatism may appear in applications as optoelectronic and sensing devices soon.

Here we utilize two organic building molecules, i.e., 5, 7-octadecadiynoic acid (OCDA) and p-xyxylenediamine, to synthesize PDA nanomaterials with excellent chromatic reversibility under environmental stimuli. As compared to the difficulty in synthesis of organic/inorganic hybrid precursors in Refs. [29] and [30], these two precursors are available commercially, and are very inexpensive. The p-xyxylenediamine serves as an amphiphilic structure-directing agent for the eventual supramolecular nanocomposite and OCDA functions as monomeric precursors of the conjugated polymer, PDA. The initial solution is composed of THF solvent, p-xyxylenediamine, and OCDA. Subsequent cooling and solvent evaporation during cast coating onto glass substrates decreases OCDA solubility, and drives self-assembly of OCDA/p-xyxylenediamine complexes into spatially-defined nanocomposites based on head-group interactions and π - π stacking. If the monomer is properly aligned, UV or γ irradiation will cause topochemical polymerization of the colorless, reactive diacetylenic groups to form blue PDA/p-xyxylenediamine nanocomposites, that retain the original mesostructure. The advantages of this technique include: ease of processing of the initial solution to directly coat a desired surface with spin coating, dip coating, or inkjet printing techniques [31], ease of forming PDA with reversible color, and synthetic flexibility.

Experimental

Fabrication of OCDA/p-xyxylenediamine films

An OCDA/THF solution (10 mg/mL) was filtered to remove any PDA present and subsequently mixed with a p-xyxylenediamine/THF solution (10 mg/mL). A typical synthesis utilized a molar ratio of 1.07/1 for NH_2 groups in p-xyxylenediamine to COOH groups in OCDA.

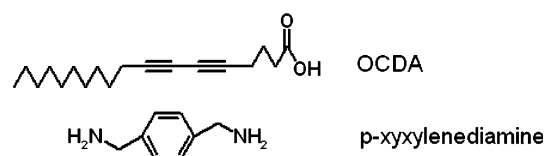


Fig. 1 Chemical structures of two building molecules

The mixture solution was either spin-coated onto glass slides using a Specialty Coating Systems P-6000 spin coater, or cast onto glass slides allowing slower THF evaporation. All solutions and slides were protected from light by covering with opaque materials.

Synthesis of PDA/p-xyxylenediamine films

As-prepared OCDA/p-xyxylenediamine thin films were irradiated from minutes to hours with UV light from a Blak Ray[®] Long Wave Ultraviolet lamp (model B 100 AP), placed 17 cm from the slide. Formation of PDA was noted by a blue color change. Subsequent heating of the film caused a reversible blue-red transition (Fig. 1).

Characterizations

The morphology was characterized by JEOL 6300FXV high resolution scanning electron microscopy (SEM). The transmission electron microscopy (TEM) images were taken using a JEOL 2010 microscope operated at 120 kV. The mesostructure was characterized with X-ray diffraction (XRD) scans obtained with a Phillips Xpert X-ray diffractometer (Cu $K\alpha$ radiation at $\lambda = 0.1542$ nm), that had been modified with a controlled heat lamp for temperature control. The nanocomposites were examined using a Beckman[™] DU 640B Ultraviolet–visible (UV–vis) spectrophotometer, and a Thermo Nicolet Nexus[™] 670 Fourier transform infrared (FTIR) spectrophotometer, with a Smart MIRacle[™] horizontal attenuated total reflectance Ge crystal accessory. Thermal analysis was conducted on a differential scanning calorimeter (DSC) by TA instruments running at 10 °C/min from 30 to 225 °C.

Results and discussion

Synthesis of nanocomposite films

Colorless 5, 7-octadecadiynoic acid/p-xyxylenediamine nanocomposite films were previously prepared by coating their mixture solution in THF on glass substrates, followed by evaporation of the solvent at room temperature. Fourier

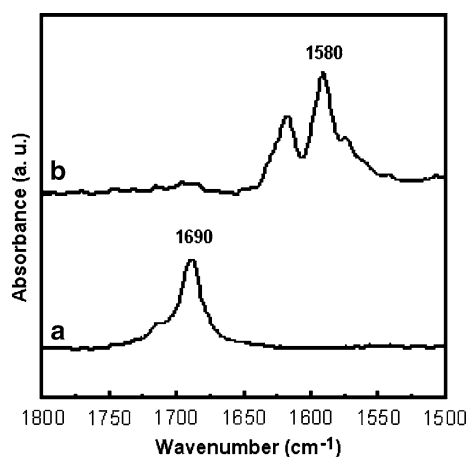


Fig. 2 Fourier Transform Infrared spectra of pure 5, 7-octadecadiynoic acid (a) and 5, 7-octadecadiynoic acid/p-xyxylenediamine complexes (b) in THF solutions

Transform Infrared spectroscopy (Fig. 2) indicates the complexation between the acid and base at a NH_2/COOH molar ratio of 1.07/1. The COOH peak for the acid monomer at $1,690\text{ cm}^{-1}$ is replaced by an asymmetric COO^- stretch at $1,580\text{ cm}^{-1}$ in the complexes [32]. This complete acid–base complexation between two building molecules is important for the structural and chromatic reversibility of this system. Exposing the colorless film to UV ($\lambda = 450\text{ nm}$) or γ irradiation causes topochemical polymerization of the incorporated diacetylinic moieties, producing blue PDA/p-xyxylenediamine nanocomposites that retain the original mesostructure [30, 33]. A SEM image shows the formation of uniform films (Fig. 3a). TEM analysis (Fig. 3b) indicates a highly ordered lamellar structure in the film with an interlamellar distance of 3.7 nm, which can be related to the collective length of bridging organic units for the 5, 7-octadecadiynoic acid and p-xyxylenediamine. X-ray diffraction analysis (Fig. 3c) further confirms the ordered lamellar structure of the nanocomposite film with a d-spacing of 3.6 nm. This value agrees well with that obtained from TEM observation. Note

that both spin coating and casting approaches produce films with the same lamellar structure and chromatic property. Nevertheless, more uniform films can be synthesized by spin coating than those by direct casting. The nanocomposite films had also been fabricated on silica. Similar to the glass substrate, films with the same structure were observed, so here, we mainly study the PDA nanomaterial on glass.

Reversible thermochromatism

An increase in temperature causes the blue PDA/p-xyxylenediamine nanocomposite to undergo a blue \rightarrow red chromatic transition due to an increase in the HOMO–LUMO spacing of the delocalized π electrons along the PDA backbone [20]. This color change is caused by polymer side chain reordering [22], that either decreases the polymer conjugate length [34], or reduces the π – π stacking between adjacent chains [19]. In present system, PDA films undergo a reversible color change from blue to red as the temperature is varied between $25\text{ }^\circ\text{C}$ and $55\text{--}68\text{ }^\circ\text{C}$. Figure 4a shows the typical photographs of different color stages in a cycle of $25\text{--}65\text{--}25\text{ }^\circ\text{C}$. The chromatic reversibility is further confirmed by the UV–vis spectra. During the heating process, the intensity at 669 nm , characteristic of the blue film (solid blue line in Fig. 4b), quickly decreased and disappeared in minutes; at the same time, a new peak at 541 nm , attributed to red color appeared, and the intensity increased (red line in Fig. 4b). Once cooled down to room temperature, the red film returns to the original blue with the disappearance of the red peak, and re-appearance of the blue peak (dashed blue line in Fig. 4b). Heating this sample above $68\text{ }^\circ\text{C}$ results in an irreversible peak change, i.e., the color change is not reversible.

It was reported that high temperatures might destroy the ordered structure of PDA assemblies through non-covalent interaction [35]. Further insight into this thermochromatic

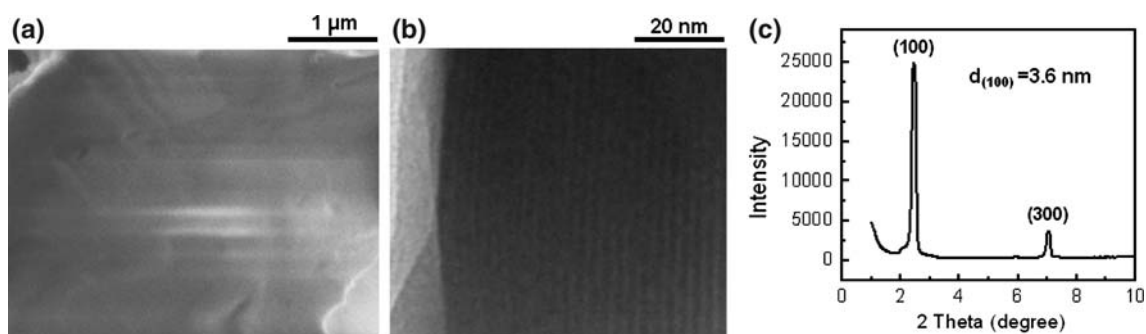


Fig. 3 Scanning electron microscopy (a), transmission electron microscopy (b), and X-ray diffraction (c) analysis of the PDA/p-xyxylenediamine nanocomposite

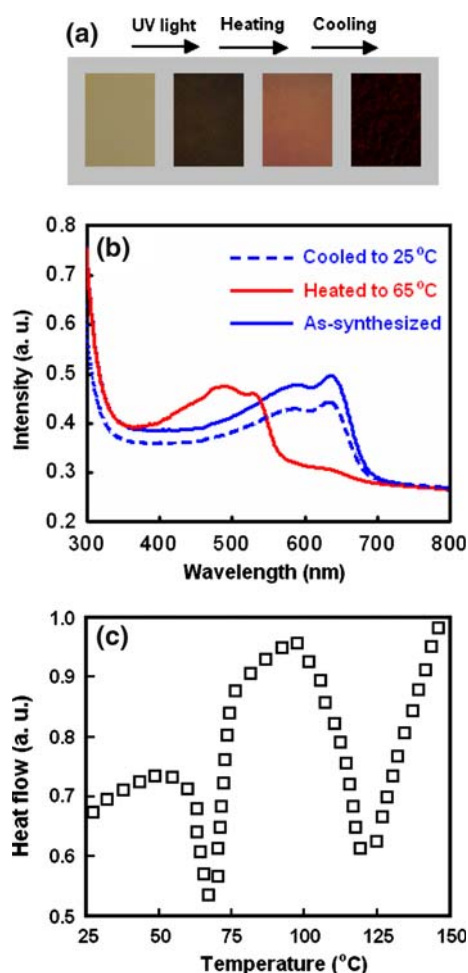


Fig. 4 PDA/p-xyxylenediamine films with reversible thermochromatism: (a) Photos for different color stages of the reversible process (heated to 60 °C, then cooled down to 25 °C), (b) typical UV–vis spectra of the blue and red films, (c) differential scanning calorimetry (DSC) of the PDA/p-xyxylenediamine film

Fig. 6 Schematic of the synthesis, structural and chromatic transition of PDA/p-xyxylenediamine nanocomposites

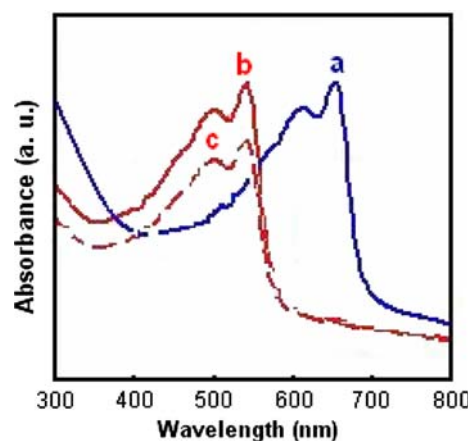
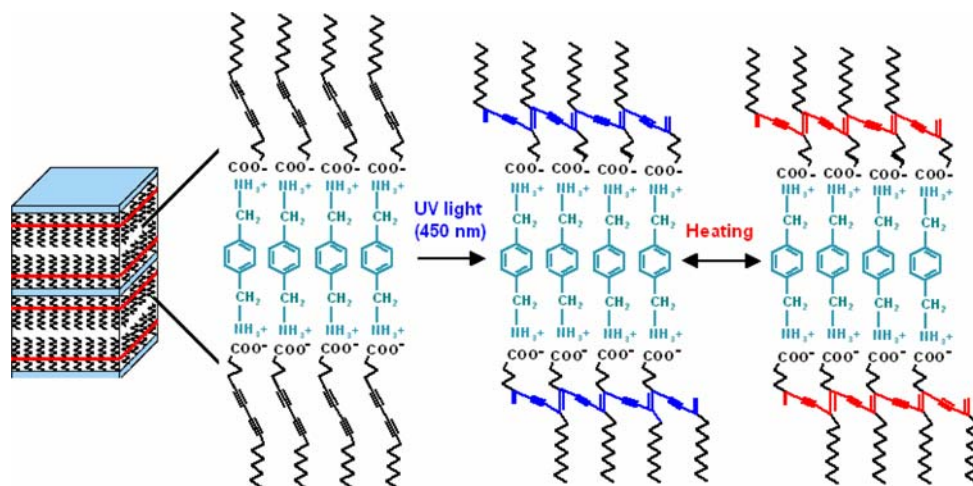


Fig. 5 UV–vis spectra of the PDA/p-xyxylenediamine film under the stimulation of THF: (a) Before exposure, (b) exposed to THF, and (c) after removal of THF

transition is possible with DSC. Figure 4c represents a typical DSC trace for the PDA/p-xyxylenediamine nanomaterial. The temperature transition at ~ 68 °C is attributed to the onset of disordering processes of the incorporated diacetylenic units, while the ordered arrangement of the lamellar network structure is maintained. The nanocomposites show reversible thermochromatism below this transition temperature [30]. The higher transition peak of the DSC spectrum is characteristic of the melting of the nanocomposite.

Solvatochromatic response

Exposure of the blue PDA/p-xyxylenediamine films to various solvents (e.g. THF, DMF, acetone, and ethanol) causes an irreversible solvatochromatic response. Figure 5 shows the typical UV–vis spectra when exposed to THF, and after removing THF. The film keeps red after removal

of the solvent. In addition, blue films switch to the red phase under strong acid condition ($\text{pH} \leq 2$), and remain blue at $\text{pH} > 2$.

Conclusions

Figure 6 summarizes the fabrication and color change of PDA/p-xyxylenediamine nanocomposite films. 5, 7-octadecadiynoic acid/p-xyxylenediamine films are first synthesized by ionic complexation and π - π stacking of building molecules in THF solutions, followed by evaporation of the solvent. Due to the highly ordered lamellar structure in above films, diacetylene moieties easily polymerize under UV light to form blue polydiacetylenes. The resultant polydiacetylenic films change their color responding to external stimuli. Under heating, the nanocomposites change their colors between blue and red rapidly and reversibly, and such a reversible color switch can proceed for many times. These materials may be applied as optoelectronic and sensing devices.

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