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Influences of solvent media on chain organization and thermochromic behaviors of polydiacetylene assemblies prepared from monomer with symmetric alkyl tails

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ABSTRACT

This contribution investigates thermochromic behaviors and morphologies of polydiacetylene(PDA) assemblies prepared from a diacetylene monomer constituting symmetric alkyl tails. Properties of solvent media strongly affects molecular organization during the preparation process. The use of water provides PDA assemblies with irregular shape while a sheet-like structure forms in butanol. Thermal analysis and X-ray diffraction detect the variation of crystalline fraction and interlamellar spacing in these structures. The change of solvent media significantly affects their thermochromic behaviors. Thin film of PDA assemblies prepared in butanol exhibits reversible thermochromism with much higher color-transition temperature compared to the system of water.

Introduction

Polydiacetylene(PDA) is an interesting class of materials that can undergo color transition upon exposure to various external stimuli such as temperature, chemicals or biomolecules [1–21]. The PDA also exhibits colorimetric response to electrical stimulus when combined with carbon nanotube [13,22]. Scientific communities have made tremendous efforts developing PDA-based materials for various applications. For example, the PDAs with reversible thermochromism can be utilized in a new type of display technology [23,24]. It can also be used to monitor local temperature of integrated circuit chip and determine authenticity of important products or documents [25–27]. Some research groups propose the utilization of PDAs in solar cell technology [28,29]. Various types of optical gas sensors have been developed based on the chromatic response of PDAs [2,3,5,6]. The color transition of PDAs generally involves segmental rearrangement within the assemblies, which in turn disrupts the conjugation length of conjugated backbone [30,31]. The perturbed PDAs change color as a result of HOMO-LUMO energy gap widening. The commercially available PDAs constituting carboxylic head group normally change color irreversibly from blue to red [32–36]. However, the specific design of PDA structure can allow different types of color transition such as blue to purple, purple-to-red and red-to-yellow [37–40].

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PDA assemblies is generally prepared by dispersing diacetylene (DA) monomer in aqueous medium followed by an incubation in a refrigerator for an extended period of time. The commercially available diacetylene(DA) monomer, 10,12-pentacosadiynoic acid (PCDA), forms vesicular structure in this environment [34,35]. UV light irradiation of the well-organized PCDA monomers triggers the topotactic polymerization process resulting in a metastable blue phase of poly(PCDA) assemblies [30,31]. It is known that increasing the temperature of poly(PCDA) above 55 °C causes an irreversible blue-to-red color transition [33–36]. This irreversible thermochromism of poly(PCDA) mainly results from the relatively weak inter- and intrachain interactions within the assemblies. To extend the utilization of PDAs in various applications, many research groups have attempted to control the color-transition temperature and also reversible thermochromism of PDAs. A common route generally involves chemical modification of PDA structure [4,33,37–45]. The effects of PDA functional head group, number of head group, diacetylene position, and alkyl chain length have been investigated. A control over color-transition behaviors can also be achieved by adding various types of materials such as alcohols [16], polymers [2,6,8,15,17], cations [19,30,46,47] and ZnO nanoparticles [18,35,36,48–50].

Recently, our co-authors have synthesized various mono- and diamides derivatives of PCDA [38–40]. Their color-transition temperature and thermochromic reversibility vary with number of amide groups and structure of the chemical linkers. The PDA assemblies prepared by using methylenediamide PCDA derivatives exhibit reversible thermochromism in aqueous suspension attributed to the enhanced inter- and intrachain interactions within the system. However, structure of this class of DA monomer constitutes two symmetric alkyl side chains while polar segment locates at the center. In polar medium, this type of geometry can hinder molecular arrangement required for topotactic polymerization of the DA monomer [42]. In fact, it was observed that the use of water as a medium for this class of DA monomer provided relatively small amount of PDAs. We hypothesize that the variation of solvent polarity may facilitate the molecular organization, leading to the higher percent conversion into PDA.

In this study, we investigate the self-assembling behaviors and photophysical properties of PDA assemblies prepared from *N*,*N*′-ethylenebispentacosa-10,12-diynamide (EBPCDA-2DA). The structure of this DA monomer illustrated in Fig. 1 constitutes polar amide head groups at center and two nonpolar alkyl tails. We have found that the use of water and butanol as solvent media during the preparation process significantly affects their chain organization and thermochromic behaviors. The local molecular arrangement within each system is explored by various techniques including UV–vis absorption spectroscopy, electron microscopy, thermal analysis, X-ray diffraction and infrared spectroscopy.

Experimental

The EBPCDA-2DA monomer was synthesized as described in literature [38]. Thermal properties of DA monomer and PDA assemblies were investigated by using differential scanning calorimeter (DSC) (Mettler Toledo DSC1). The DA monomer were purified by recrystallization process prior to the DSC measurement. The samples of PDA assemblies were prepared by drop-casting on Petri dish and dried in vacuum oven at room temperature for one day. About 3–5 mg of sample was encapsulated in aluminum pan and measured under nitrogen gas using 5 °C/min heating and cooling rate. The melting point was measured at peak position.

The PDA assemblies were prepared by dissolving DA monomer in chloroform and then filtered by using a 0.45 μm nylon filter to remove residual polymers. The solvent was slowly removed by heating at 60 °C in water bath. The deionized water or butanol was added to provide 0.5 mM concentration. The samples were sonicated at about 80 °C for 90 min to disperse DA monomers into the solvent media. The suspension was allowed to cool down to room temperature and then kept at 4 °C overnight to induce the self-assembling process. The cloudy suspensions of DA assemblies were irradiated with UV light (10 W, $\lambda \sim 254$ nm) for 2 min, resulting in a blue color. Morphologies of the PDA assemblies were investigated by scanning electron microscopy (SEM, LEO 1455 VP). The SEM samples were prepared by dropping the PDA suspensions onto polished silicon wafers. The structure of PDA assemblies were studied by using X-ray diffractometer (Bruker AXS Model D8 Discover λ(Cu-Kα) = 1.54 Å). Samples were prepared by drop-casting onto glass slides. Local interactions within PDA assemblies were explored by utilizing infrared (IR) spectroscopy (PerkinElmer Spectrum GX). Samples were prepared by drop-casting on clean

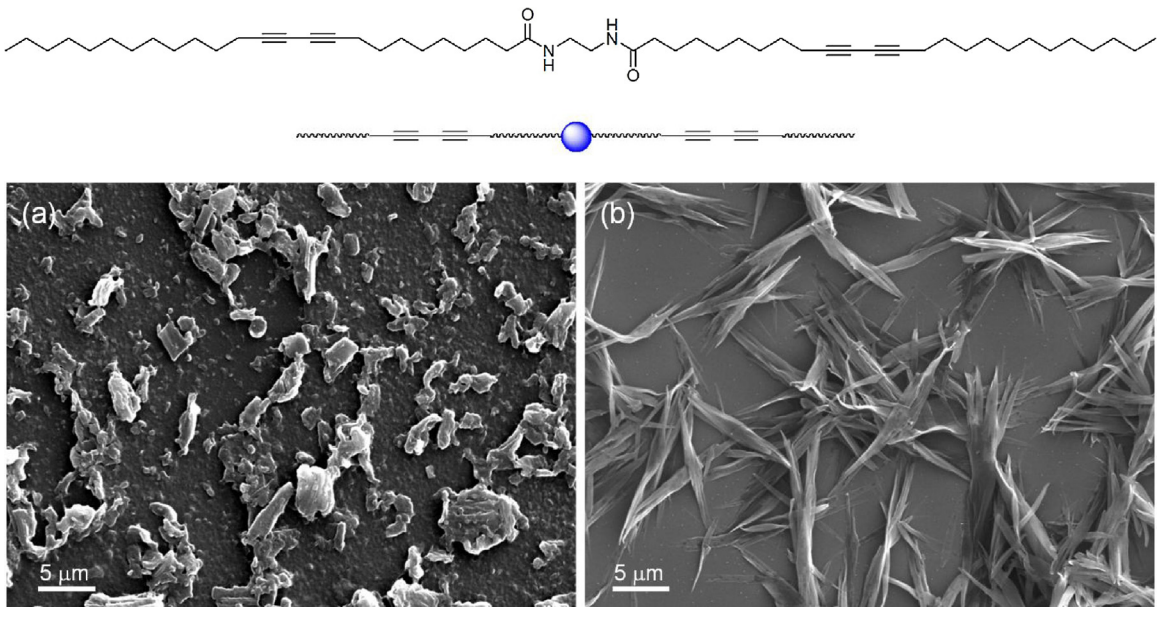

Fig. 1. (Above) Structure of EBPCDA-2DA monomer. (Below) SEM images of PDA assemblies prepared in (a) water and (b) butanol.

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