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Conjugated Polymer-Embedded Thermochromic Strip Sensors with a Tunable Colorimetric Response

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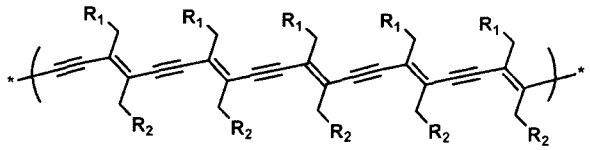
Introduction

Polydiacetylenes (PDAs), conjugated polymers, which have alternating ene-yne backbone structures, have several very intriguing properties.[1-9] First, these materials are produced by radiation (UV or γ-ray)-induced polymerization of molecularly-assembled diacetylene (DA) monomers without the need for chemical initiators or catalysts. Second, these polymers generally have an intense blue color corresponding to maximum absorption wavelengths of *ca.* 640 nm. Lastly, the blue-colored PDAs undergo color transitions to form a red phase in response to several types of environmental stimulations such as heat (thermochromism), solvent (solvatochromism), mechanical stress (mechanochromism), and molecular recognition (affinochromism).[10-18]



Polydiacetylene

PDAs have been prepared in the form of nano/micro particles in aqueous solvent,[13] thin molecular layers on solid substrates,[10] nanotubes/nanowires,[19,20] bulk powders[1] as well as silica composites[3] and electrospun microfibers.[21] Recently, we reported a new approach for creation of PDA supramolecules in polymer matricies.[22] A flexible PDA strip sensor was readily obtained by employing a simple mixing and drying procedure. Drying of a suspension containing PDA vesicles and poly(vinyl alcohol) (PVA) in a Petri dish afforded a thin polymer film, which undergoes a blue-to-red color transition promoted by thermal stress. Thus, the blue-colored PVA film at 25 °C becomes purple at 60 °C and eventually changes to red above 70 °C. An interesting issue with regard to these flexible PDA strip sensors is whether the color changing temperature of films of this type can be controlled by employing different types of DA monomers. If so, the colorimetric temperature window of PDA can be significantly expanded and manipulated. As part of our continuing efforts in this area aimed at the development of PDA-based functional materials,[21-28] we have uncovered a strategy of rationally designing thermochromic strip sensors with tunable colorimetric responses.

The five structurally different diacetylene monomers, shown in Figure 1, were selected for the purpose of making colorimetrically responsive strip sensors. In our earlier studies with DA supramolecules, we observed that strong head-group interactions in vesicles causes the resulting PDAs to be colorimetrically more stable upon thermal stimulation.[29] As a result, the bolamphiphilic DA monomer, DCDDA-bis-mBzA **1** that has four hydrogen-bondable groups (two amides and two carboxylic acids) and two phenyl groups is expected to produce PDAs with enhanced thermal stability. The 3-aminobenzoic acid-derived DA PCDA-mBzA **2** should enable us to test the influence of a single head group, compared with DCDDA-bis-mBzA **1**, on the colorimetric stability.

The next system should enable us to probe the effects of aromatic interactions on colorimetric stability. Compared with PCDA-mBzA **2**, the aminobutyric acid-derived PCDA-ABA **3** has a similar distance between the amide and the terminal carboxylic groups but it does not contain a phenyl ring. The DA monomer PCDA-EDEA **4** has an internal

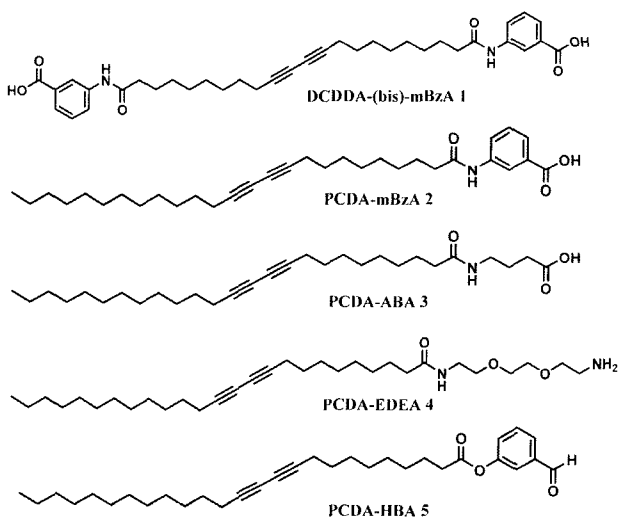


Figure 1. Structures of DA monomers investigated in this study.

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amide group and a terminal amine group. In contrast with PCDA-ABA **3**, the hydrogen bonding ability of the terminal amine group in PCDA-EDEA **4** is expected to be weaker than that of terminal carboxylic group in PCDA-ABA **3**. PDAs prepared from PCDA-HBA **5**, a 3-hydroxybenzaldehyde derivative, are expected to display the most sensitive response to thermal stress since they do not contain any functional groups capable of hydrogen bonding.

Experimental

Materials. Poly(vinyl alcohol) (Mw=89,000-98,000, 99+% hydrolyzed), oxalyl chloride, and 3-hydroxybenzaldehyde were purchased from Aldrich. 10,12-Pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals. Preparation of DCDDA-bis-mBzA **1** is reported elsewhere.[29] PCDA-mBzA **2**, PCDA-ABA **3**, and PCDA-EDEA **4** were previously reported.[23]

Synthesis of PCDA-HBA 5. To a solution containing 1.00 g (1.33 mmol) of 10,12-pentacosadiynoic acid in 20 mL of methylene chloride was added dropwise 1.02 g (7.98 mmol) of oxalyl chloride and a catalytic amount of DMF at room temperature. The resulting solution was stirred at room temperature for 2 h, concentrated *in vacuo*, and the residue was redissolved in 5 mL of THF. The resulting solution was added dropwise to the solution containing 0.65 g (5.32 mmol) of 3-hydroxyaldehyde in 10 mL of pyridine. The resulting mixture was allowed to stir overnight at room temperature and poured into cold water. The desired DA monomer PCDA-HBA **5** was precipitated out as a solid (0.41 g, 62.3%).

PCDA-HBA **5**: m.p 44 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ=0.88 (t, 3H), 1.25-1.56 (m, 34H), 1.76 (quint, 4H) 2.25 (t, 4H), 2.59 (t, 2H), 7.37 (d, 1H), 7.55 (d, 1H), 7.60 (d, 1H), 7.76 (d, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ=14.10, 19.15, 22.66, 24.76, 28.23, 28.30, 28.69, 28.81, 28.85, 29.00, 29.03, 29.06, 29.31, 29.44, 29.57, 29.59, 29.61, 31.88, 34.22, 65.14, 65.27, 77.36, 77.60, 122.26, 127.21, 127.78, 130.07, 137.66, 151.24, 171.94, 191.18; IR (NaCl, cm^{-1}) 2970-2920, 2848, 2740, 1751, 1700, 1589, 1461.

Preparation of DA Suspensions. The DA monomer was dissolved in chloroform and the organic solvent was removed by purging with N_2 to generate a thin lipid film on the glass surface. Deionized water was added to yield a total monomer lipid concentration of ca. 2.0 mM. In the case of a chloroform insoluble DA, the monomer was dissolved in a minimum amount of DMF and the resulting solution was injected into deionized water to make a desired lipid suspension. The sample was then heated at 80 °C for 15 min and probe-sonicated for 15 min. The resulting solution was filtered through a 0.8 μm filter and the filtrate was cooled at 4 °C for 12 h.

PDA-Embedded PVA Film. An aqueous suspension (ca. 2 mM, 6 mL) containing moleculary-assembled DAs was mixed with an aqueous PVA solution (10 wt%, 4 mL) with stirring. The resultant mixture (4 mL) was cast into a Petri dish (diameter 6.5 cm) and dried at 30 °C for 2 d (or at room temperature for 5 d). During the drying process, the solutions were protected from light. The dried films were irradiated by 254 nm UV light (1 mW/cm^2) until saturation of blue color and the resultant blue-colored film was peeled from the dish.

Results and Discussion

Preparation of PDA-Embedded PVA Films. Embedment of PDA supramolecules in PVA films was carried out by using a mixing-drying process. The typical method is shown pictorially in Figure 2. A DA monomer was subjected to routine procedures to transform the DA lipid monomer to self-assembled DA vesicles in aqueous solution (see Experimental). The DA vesicle solution was mixed with an aqueous 10% PVA solution (6 : 4, vol%), then casted in a Petri dish (diameter: 6.5 cm) and dried at 30 °C for 2 d (or at room temperature for 5 d). Polymerization was carried out at room temperature by irradiating with 254 nm UV light (1 mW/cm^2) of the PVA films-embedded with molecularly-assembled DAs. Typical blue-colored films (200-400 μm thickness) were obtained with all of the mono-

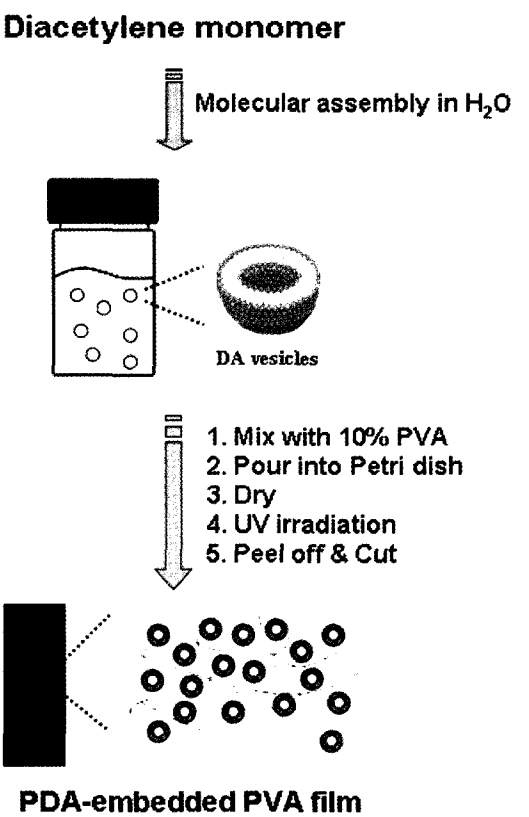

Figure 2. Procedure for the fabrication of a PDA-embedded PVA film.

mers.

The critical issue related to the preparation of PDA-embedded PVA films is that the integrity of the self-assembled DA monomers should not be affected during the PVA film making process. If PVA disrupts the structurally well-ordered nature of the DA assembly, this would directly affect the polymerization step. Thus, the successful blue color formation after UV-induced photopolymerization of the dried film confirms that the DA monomer assembly is maintained during the preparation of the DA-embedded PVA film. This is an important observation since it indicates that PVA as a matrix polymer does not disturb the ordered structures of moleculary assembled DAs.

Thermochromism. Having prepared the PDA-embedded PVA films, we next investigated their thermally stimulated colorimetric responses. Accordingly, the PVA films were placed on a temperature-controlled hot plate and the color change was monitored while the temperature was gradually increased.

In Figure 3 are displayed photographs of PDA-embedded PVA films during the heating process. The photographs clearly show that the colorimetric response of the PVA films is highly dependent on the DA monomers used. Thus, the PVA film prepared with DCDDA-bis-mBzA **1** shows colorimetric stability until 120 °C and initiation of the color transition is observed above 130 °C. The film prepared with PCDA-mBzA **2** becomes purple at 100 °C and eventually changes to red above 120 °C.

The origin of the relative colorimetric stability of the DCDDA-bis-mBzA **1**-derived film, compare with PCDA-mBzA **2**, is attributed to the presence of stronger headgroup interactions since the carboxyphenylanilido groups are present at both ends of the DA monomer.

Removal of aromatic interactions is found to directly affect the colorimetric stability of PDAs. Accordingly, the PVA film derived from PCDA-ABA **3**, which compared to PCDA-mBzA **2** lacks a phenyl group, begins its color transition at lower temperature than that obtained with PCDA-mBzA **2**. The film displays a blue-to-purple color change at 70 °C and gradually turns to red at higher temperature.

The PVA film obtained from the amine-terminated DA PCDA-EDEA **4** has initiation of an apparent color transition at 50 °C and becomes red above 70 °C. Compared with PCDA-ABA **3**, the PCDA-EDEA **4**-derived PDA supramolecules is expected to have weaker headgroup interactions and a lower stability due to the positive charges on amine groups, developed during preparation of PDAs under slightly acidic conditions.

Finally, in the extreme case where hydrogen bonding interactions are absent, as in the polymer film derived from PCDA-HBA **5**, the color change occurs at a lower temperature than with other systems. In this case, the film becomes purple-red at 50 °C and remains that color at higher temperatures.

The results described above clearly support the proposal that stronger headgroup interactions lead to colorimetrically more stable PDA supramolecules. Thus, the PDAs derived from DCDDA-bis-mBzA **1**, which offers multiple hydrogen bonding as well as aromatic interactions, results in formation of the colorimetrically most stable PDA film. In contrast, the aldehyde-containing DA PCDA-HBA **5** yields the colorimetrically least stable supramolecular polymers.

Conclusions

In this effort, we have prepared various types of PDA-embedded PVA films and investigated their colorimetric responses to thermal stimulation. Depending on the DA monomers employed, the PDA-embedded PVA films displayed different initial color changing temperatures. In gen-

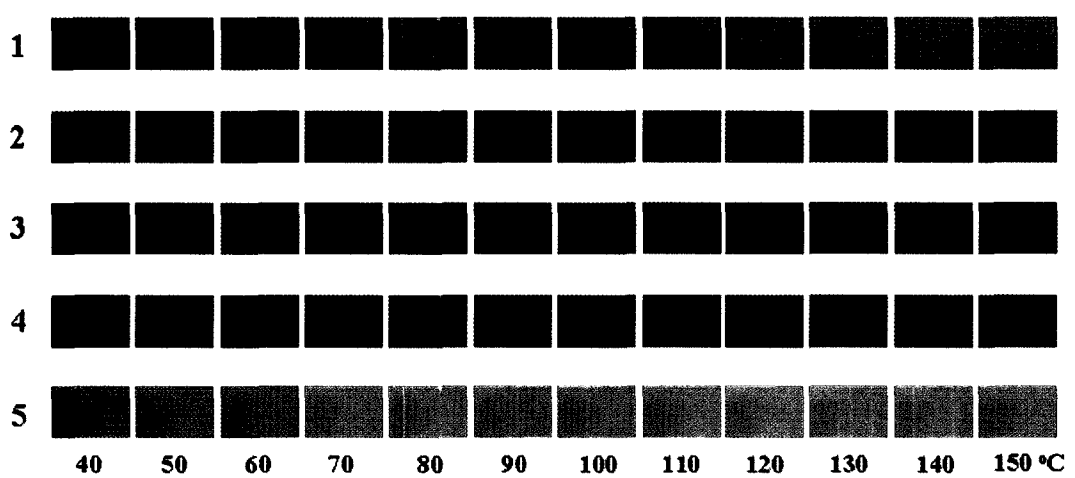

Figure 3. Photographs of PDA-embedded PVA films prepared with DCDDA-bis-mBzA (1), PCDA-mBzA (2), PCDA-ABA (3), PCDA-EDEA (4), and PCDA-HBA (5) during heating process.

eral, DA monomers capable of providing stronger headgroup interactions result in the generation of colorimetrically more stable PDA supramolecules. The observations made in the current investigation should be assist the design of colorimetrically tunable conjugated polymer-embedded polymer films.

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