Dyes and Pigments 89 (2011) 194-198

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

A thermally reversible temperature sensor based on polydiacetylene: Synthesis and thermochromic properties

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ARTICLE INFO

Article history: Received 25 October 2009 Received in revised form 5 December 2009 Accepted 7 December 2009 Available online 6 January 2010

Keywords: Polydiacetylene Temperature sensor Thermal reversibility PVA film

ABSTRACT

A novel temperature sensor based on polydiacetylene, displayed colorimetrically reversible properties in the range of 30 °C and 70 °C in solution. PVA film embedded PDA supramolecules displayed similar temperature reversibility.

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PIĞMËNTS

1. Introduction

Chemosensors [1–3] based on conjugated polymers are attractive because their absorption, emission, and redox characteristics are sensitive to environmental perturbations [4-6]. Polydiacetylenes (PDAs), a family of conjugated polymers [7-11] are generally prepared by UV irradiation of self-assembled diacetylene (DA) supramolecules. If PDAs are prepared under optimal conditions, they normally display a blue color with a $\lambda_{max} = ~{\sim}640$ nm. Most importantly, blue PDAs undergo a red shift ($\lambda_{max} = \sim 550 \text{ nm}$) upon environmental stimulation, which has led to the development of a variety of PDA-based chemosensors [12-17]. Accordingly, the colorimetric detection of biologically, chemically and environmentally important target molecules such as DNAs, viruses, proteins, metal ions, organic solvents etc. have been reported [12–17]. However, the development of molecular sensors to detect changes in "environmental" properties, such as temperature and pressure, has received very little attention. In addition, most of these chromatic responses are irreversible, and the blue to red chromatic change is irreversible when the external stimulus is removed, which limits the

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application of PDAs in colorimetric sensing. To the best of our knowledge, only a few examples of the reversible chromatic response of PDA materials have been reported [18–29].

This paper concerns a conjugated polymer based on diacetylene which carries a phenylacetamide head, the phenyl group of which, results in π - π stacking between monomers and acetamide which induces intermolecular H-bonding during self-assembly. The novel polymer displays excellent colorimetric reversibility in the range of 30–70 °C in solution; furthermore, a PDA-embedded poly(vinyl alcohol) (PVA) film shows similar colorimetric reversibility.

2. Experimental

2.1. Materials and equipments

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel 60 (230–400 mesh). Thin layer chromatography (TLC) was carried out using Merck 60 F_{254} plates with a thickness of 0.25 mm ¹H NMR and ¹³C NMR spectra were recorded using 250 MHz NMR. Mass spectra were obtained using a JMS-HX 110A/110A Tandem Mass Spectrometer (JEOL). UV absorption spectra were obtained on UVIKON 933 Double Beam UV–Vis Spectrometer.



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Scheme 1. Synthesis of monomer 1.

2.2. Synthesis

2.2.1. 2,2,2-Trifluoro-N-(4-hydroxyphenyl)acetamide

To a solution containing 2.0 g (17.7 mmol) of trifluoroacetic acid in 20 mL of CH₂Cl₂ was added 2.1 g (18.3 mmol) of *N*-Hydroxysuccinimide (NHS) and 4.2 g (20.4 mmol) of *N*,*N'*-Dicyclohexylcarbodiimide (DCC). The resulting solution was stirred for overnight at room temperature under N₂. The solvent was evaporated after the white precipitate was filtered and trifluoroacetate was removed by flash column chromatography (silica gel, eluent CHCl₃). The ensuing activated ester was added to a solution of 4-aminophenol (2.0 g, 18.3 mmol) in CH₂Cl₂ (10 mL) and the resulting mixture was stirred for 24 h. After the solvent was evaporated, the residue was purified using silica gel column (CHCl₃/CH₃OH, 100:2) to give 2,2,2-trifluoro-*N*-(4-hydroxyphenyl) acetamide (2.65 g, 69% yield) as white solid. ¹H NMR (CD₃OD, 250 MHz) δ (ppm): 7.32 (d, 2H, *J* = 12.5 Hz), 6.78 (d, 2H, *J* = 12.5 Hz); ¹³C NMR (CD₃OD, 62.5 MHz) δ (ppm): 155.43, 155.31, 127.83, 122.62, 114.99.

2.2.2. Monomer 1

To a solution containing 0.50 g (1.34 mmol) of 10,12-pentacosadiynoic acid in 10 mL of methylene chloride was added dropwise 0.55 g (4.32 mmol) of oxalvl chloride at room temperature. The resulting solution was stirred at room temperature for 3 h. To the ensuing solution was added a catalytic amount (one drop) of DMF and the mixture was stirred for one additional hour. After concentrating in vacuo, the residue was redissolved in 10 mL of methylene chloride. The resulting solution was added dropwise to a solution containing 0.29 g (1.42 mmol) of 2,2,2-trifluoro-N-(4-hydroxyphenyl)acetamide in 10 mL of THF. The resulting mixture was stirred overnight at room temperature. The solvent was removed under vacuum and the residue purified by silica gel column chromatography (CHCl₃ as an eluent) to give 0.32 g (42%) of the desired diacetylene monomer **1** as a white solid. ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.93 (s, 1H), 7.48 (d, 2 H, J = 12.5 Hz), 7.25 (d, 2 H, J = 12.5 Hz), 2.49 (t, 2H, J = 7.5 Hz), 2.20–2.16 (m, 4H), 2.17–1.65 (m, 2H), 1.44–1.19 (m, 30H), 0.81 (t, 3H, J = 6.25 Hz). ¹³C NMR (CDCl₃, 62.5 MHz) δ (ppm): 172.56, 148.32, 132.68, 122.41, 121.56, 65.30, 65.17, 34.27, 31.90, 29.62, 29.47, 29.33, 29.08, 28.87, 28.73, 28.33, 28.27, 24.79, 22.68, 19.19, 14.11. FAB MS *m*/*z* = 562.3504 [M + H]⁺, calc. for $C_{33}H_{47}O_3NF_3 = 562.3508$.

2.3. Preparation and polymerization of micelle

Preparation of PDA vesicles in aqueous solution was achieved by the following method. Diacetylene monomer (11.2 mg, 0.02 mmol) was dissolved in a small amount of DMSO (1 mL), and the organic solution was injected into 19 mL deionized water while shaking the mixed solution to yield a total monomer concentration of 1 mM. The sample was sonicated at 80 °C for 25 min and the resulting solution was filtered through a 0.8 μ m filter and the filtrate cooled at 4 °C for 12 h. Polymerization was carried out at room temperature by irradiating the solution with 254 nm UV light (1 mW/cm^2) for 5 min.

2.4. Color reversibility (CR) values

For thermochromic properties experiments, all UV spectroscopy measurements were carried out using a 1 cm optical path length cell. The blue polymer was first transformed to a purple phase using a heating—cooling cycle. UV—Vis spectra were collected from the second cycle. To quantify the extent of the purple-to-red transitions within the polymer, the % color reversibility (CR) was calculated using the following equation [30]:

$CR = [(PB_0 - PB_1)/PB_0] \times 100$

where $PB = A_{blue}/(A_{blue} + A_{red})$, A_{blue} and A_{red} are the absorbance values at 625 nm and 535 nm in the UV–Vis spectrum, respectively. PB_0 and PB_1 are pre- and post-thermal perturbations values, respectively. The different temperature of PDA solution was controlled by a water-bath system.

2.5. Fabrication of PDA-embedded PVA film

A 5 mL of self-assembled DA aqueous solution (ca. 1 mM, 5% DMSO) was mixed with an aqueous PVA solution (10 wt %, 5 mL) with stirring. The resultant mixture solution was cast into a Petri dish (diameter 6.5 cm) and dried at room temperature for five days. During the drying process, the solutions were protected from light. The resulting transparent film was irradiated with 254 nm UV light to induce polymerization. The heating or cooling of film by a waterbath system can lead to desired temperature.



Fig. 1. Photographs of different color stages at 30 °C and 70 °C.





3. Results and discussion

3.1. Synthesis monomer and preparation of polymer

The synthetic route of monomer **1** was shown in Scheme 1. Firstly, 2,2,2-trifluoro-*N*-(4-hydroxyphenyl)acetamide 2 was synthesized through the NHS-activated trifluoroacetic acid and 4aminophenol. Then, the reaction of **2** and SOCl₂-activated 10,12pentacosadiynoic acid afford the final product **1**. The synthesized monomer **1** was characterized through the data from ¹H NMR, ¹³C NMR and FAB Mass spectra. These characterizations confirmed the formation of monomer **1**. The DA monomers were then converted to PDA supramolecules via a routine procedure. UV irradiation of the suspensions derived from self-assembled monomers for 5 min resulted in the formation of stable and blue-colored PDA molecules (Scheme 2).

3.2. Thermochromism of polymer in solution

Fig. 1 shows the photographs of different color stages at 30 °C and 70 °C. In present system, PDA solution undergoes a color change from blue to red when the temperature initially increased to 70 °C. When the temperature decreases to 30 °C, the color of PDA solution change to purple. The steric hindrance introduced between side chains could relax with a thermodynamic process during the first heating step ranging from room temperature to 70 °C. In this thermochromic phase (from blue to red), the slight reorganization of the aliphatic side chains may produce a slight torsion of the aromatic backbone with a less effective conjugation. The further heating-cooling cycle showed the reversible transformation between purple and red in the range of 30-70 °C. Fig. 2 shows absorbance spectra of



Fig. 2. Top: UV-Vis spectra of PDA solution during heating (a) and cooling (d) procedures. Bottom: Colorimetric response value (CR) changes during a heating-cooling cycle.

PDA solution at different temperature during heating and cooling procedures. When the temperature was increased to 70 °C, the solution became red, while the absorbance at 625 nm decreased and 535 nm increased. The purple color and absorbance at 625 nm were recovered when the sample was cooled to 30 °C. The representative percentage colorimetric response values (CR %) were calculated from the visible spectra recorded for PDA solution for different temperature. CR is a parameter reflecting the change in the visible spectrum after heating or cooling the colorimetric polymers. During the heating process from 30 °C to 70 °C, the CR value was enhanced gradually, means the transformation from purple-to-red color with temperature increasing. Once cooled down to 30 °C, the red PDA solution returns to the purple with CR value decreasing. Accordingly, repeated heating-cooling cycles can lead to the switches between red and purple colors (Fig. 3).

Although considerable research effort has been devoted to elucidating the reason of color changes in PDA materials caused by environmental stimulus, the exact mechanism of the blue to red color transition is still not fully understood [6]. Previous results have shown that both side chain order and head group H-bonding need to be responsible for the color transition of PDA material [21–23]. The disruption of the hydrogen bonding could allow release of the strain energy imposed to the alkyl side chains generated during polymerization. The release of the side chain strain can cause partial distortion of the arrayed p-orbitals, leading to the decrease of the effective conjugation length of the polymer [31]. Strong head



Fig. 3. The UV–Vis spectra (a) and colorimetric response value (b) changes in thermal cycles of polymer between 30 $^\circ C$ and 70 $^\circ C.$



Fig. 4. Color switches of PDA-embedded PVA film with temperature changes.

group interactions are found to be required in order to provide PDA molecules with the ability to recover their initial molecular structures. In this work, the introduction of phenylacetamide head into PDA derivative enhance intermolecular interaction (including $\pi - \pi$ stacking from phenyl groups and hydrogen bonding from amide groups) between side chains, resulting in the formation of reversible thermochromic properties and enhanced thermal stability.

3.3. Thermochromism of polymer in PVA film

To explore the thermal reversibility of PDA polymer in solid phase, the PDA-embedded PVA film was fabricated and thermochromic behavior was investigated. Embedment of PDA supramolecules in PVA films was carried out by a mixing-drying process. During the drying process, the solutions were protected from light. The resulting transparent film was irradiated with 254 nm UV light to induce polymerization. The blue-colored PVA film embedding with PDA polymer was then peeled from the dish. As shown in Fig. 4, the film initially undergoes a transformation from blue to purple color after a heating-cooling cycle. Further reversible color changes between red and purple can be observed when was heated to 70 °C and cooled to 30 °C. The color-changing properties of PDA-embedded PVA film and PDA solution are similar. Notablely, too high temperature (>80 °C) will lead to irreversible thermochromic behavior of PVA film embedded PDA molecules.

4. Conclusions

A new conjugated polymer based on diacetylene was synthesized and thermochromic behavior was investigated. In present system, PDA solution showed a reversible color change from purple-to-red as the temperature is varied between 30 °C and 70 °C, and repeated heating-cooling cycles can lead to the switches between red and purple colors. Furthermore, reversible thermochromic behavior was demonstrated in the PVA film embedded PDA molecules.

Acknowledgements

This research was supported by collaboration fund between Korea and China (KOSEF; F01-2008-000-10026-0, Chinese NSFC; 50811140342), Seoul R&BD Program (10816) and WCU program (R31-2008-000-10010-0).

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