



Original article

A thermally reversible supramolecular system based on biphenyl polydiacetylene



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ARTICLE INFO

Article history:

Received 18 March 2015

Received in revised form 30 April 2015

Accepted 11 May 2015

Available online 28 May 2015

Keywords:

Polydiacetylene

Head group

Self-assembly

Reversible

ABSTRACT

A new type of diacetylene monomer which includes a biphenylcarboxylic acid group as its head group is synthesized. Polymerization was performed after monomer form spherical vesicle by self-assembly in the water. The polydiacetylene displayed completely thermochromic color change in the range of 20–95 °C owing to the presence of strong π – π interaction caused by biphenyl group and hydrogen bonding between head group.

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1. Introduction

Conjugated polymers have been greatly investigated because of its unique optical and electric properties which can be attributed to its extensively delocalized π -electron networks [1–5]. Their delocalized backbone make their absorption and emission properties very sensitive to the environmental perturbation, which make them become progressive candidates for various biological and chemical chemosensors [6–12]. Polydiacetylenes (PDAs) are very interesting materials among conjugated polymers [13–19]. PDAs are readily prepared by UV irradiation of self-assembled diacetylene supramolecules without need of any initiators or catalysts. Consequently, there are no unwanted by-product and impurity in the resulting polymer. Well-designed DA monomer could be easily polymerized in aqueous solution in the form of nanostructured liposomes or vesicles because of their amphiphilic property. The PDAs could go through colorimetric transition caused by the external stimuli such as heat (thermochromism) [20–23], solvent (solvatochromism) [24–26], mechanical stress (mechanochromism) [27–29] and ligand–receptor (affinochromism) [9,30–32] interaction.

Many investigations have been made on the thermochromism of PDAs. Although some PDA system displayed reversible thermochromism, but in most of the cases reported earlier, reversible thermochromism was observed only in the narrow temperature range, for example 25–55 °C [33], or they were not fully reversible as they deteriorate to violet to red rather than blue to red after first heating–cooling cycle [34]. In the investigation described below, we prepared a new polydiacetylene, (Bip-PDA), in which biphenylcarboxylic acid group is connected in its side chain, the biphenyl group provides strong aromatic interaction between monomers and carboxylic acid induces intermolecular H-bonding during self-assembly. The new polydiacetylene displays completely reversible thermochromism in the range of 20–95 °C in solution.

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 (200–300 mesh). The laser light scattering particle size measurements were performed on a ALV/CGS-5022F. ¹H NMR and ¹³C NMR spectra were recorded using Bruker AVANCE 500 MHz. Mass spectra were obtained using a Micromass GCTM Time-of-Flight Mass Spectrometer. UV irradiation was performed by LUYOR LEC-180L hand lamp. Probe sonication was carried out by using Fisher Sonic dismembrator

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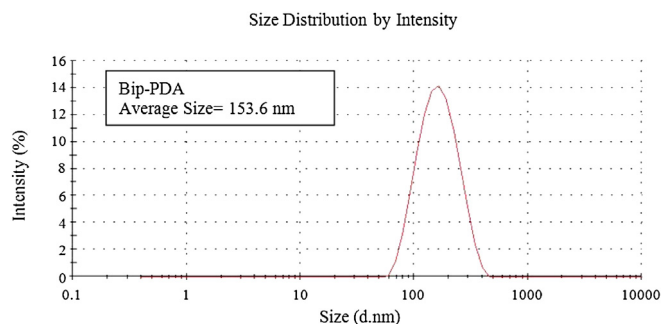


Fig. 1. Size distribution of PDA sol obtained from laser light scattering.

model 550. UV absorption spectra were obtained on UVIKON 933 Double Beam UV-vis Spectrometer.

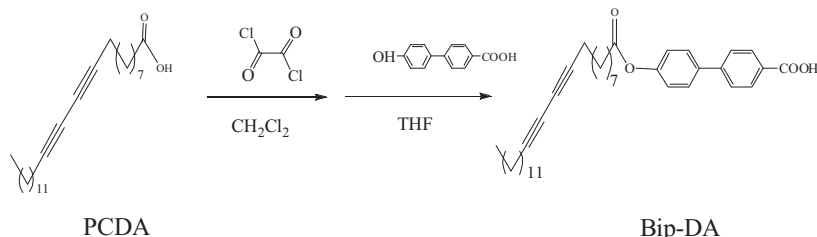
2.2. Synthesis of Bip-DA

Oxalyl chloride (0.61 mL, 7.15 mmol) was added dropwise to a methylene chloride solution containing 0.702 g 1.87 mmol) of 10,12-pentacosadiynoic acid (PCDA) at room temperature. The resulting mixture was stirred for 30 min and then one drop of fresh DMF was added as catalyst. Above solution was stirred at room temperature for another 5 h. Residue obtained by concentration of the above solution dissolved in 20 mL THF, then added dropwise a solution containing 0.403 g (1.88 mol) 4'-hydroxy-4-biphenylcarboxylic acid and 0.4 mL (2.89 mmol) of triethylamine. The resulting solution was stirred overnight at room temperature under N_2 . The solvent was removed under vacuum and the residue purified by silica gel column chromatography (CH_2Cl_2 100%) to give the desired diacetylene monomer, Bip-DA 0.93 g, 87%), as a white solid. ESI-MS: m/z 570.3709 $[M]^+$. 1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, 2H, $J = 8.2$ Hz), 7.65 (d, 2H, $J = 8.3$ Hz), 7.62 (d, 2H, $J = 8.5$ Hz), 7.17 (d, 2H, $J = 8.5$ Hz), 2.56 (t, 2H, $J = 7.4$ Hz), 2.22 (m, 4H), 1.79–1.71 (m, 2H), 1.53–1.45 (m, 4H), 1.42–1.19 (m, 26H), 0.85 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.17, 170.53, 150.85, 145.43, 137.41, 130.64, 128.27, 128.03, 127.00, 122.04, 77.55, 65.26, 65.13, 34.30, 31.82, 29.60, 29.54, 29.24, 28.99, 28.94, 28.79, 28.76, 28.25, 28.19, 24.79, 22.58, 19.10, 14.01.

2.3. Preparation and polymerization of vesicles

The diacetylene monomer Bip-DA (11.4 mg, 0.02 mmol) was dissolved in a small amount of DMF (1 mL) and the clear solution was added to 19 mL hot deionized water dropwise to make a 1.0 mmol/L of dispersed monomer suspension. The resultant suspension was probe-sonicated at 80 °C for 25 min and the resulting solution was filtered by a 0.8 μm filter and the filtrate cooled at 4 °C for 12 h. Polymerization was performed at room temperature by irradiating the solution with 254 nm UV light (1 mW/cm²) for 15 min.

The sizes of the lipid assembled vesicles within the PDA sol were characterized by dynamic light scattering (DLS) technique.



Scheme 1. Synthesis of Bip-DA.

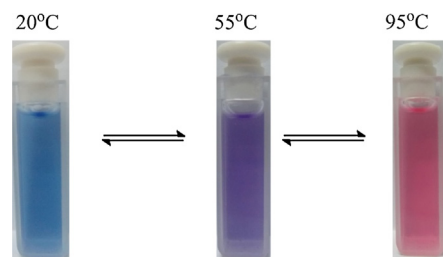


Fig. 2. Photographs of an aqueous solution of Bip-PDA at 20 °C, 55 °C, and 95 °C.

The DLS size distribution revealed that the average hydrodynamic diameter of the particles was 153.6 nm (Fig. 1).

2.4. Colorimetric response (CR) value

In order to determine thermochromic properties of the polydiacetylene we synthesized, (Bip-PDA), all UV spectroscopy measurements were carried out using a 1 cm optical path length cell. The blue polymer was first transformed to its red phase by using a heating-cooling cycle. UV-vis spectra were recorded during the first cycle. To quantify the extent of the blue-to-red transitions within the polymer, the % colorimetric response (CR) value was calculated using the following equation:

$$CR = \left[\frac{PB_0 - PB_1}{PB_0} \right] \times 100 \quad (1)$$

where $PB = A_{blue}/(A_{blue} + A_{red})$. In Bip-DA vesicle, A_{blue} and A_{red} are absorbances at 633 nm and 539 nm in the UV-vis spectrum, respectively. PB_0 and PB_1 are the respective pre- and post-thermal perturbations values. The different temperature of PDA solution was controlled by a water-bath system.

3. Results and discussion

3.1. Monomer synthesis and preparation of polymer

Bip-DA was prepared using the route shown in Scheme 1. Firstly, oxalyl chloride was treated with 10,12-pentacosadiynoic acid (PCDA) to get its acid chloride derivative. The acid chloride was then reacted with 4'-hydroxy-4-biphenylcarboxylic acid to generate Bip-DA in 87% yield after the silica column chromatography. The synthesized monomer Bip-DA was fully characterized by 1H NMR, ^{13}C NMR and ESI Mass spectra. These characterizations confirmed the formation of Bip-DA. The Bip-DA monomers were then transformed into vesicles by a routine procedure. UV irradiation of self-assembled monomers Bip-DA for 15 min resulted in the formation of stable and blue-colored PDA sol.

3.2. Thermochromism of Bip-PDA in solution

Fig. 2 shows images of a vial containing an aqueous solution of Bip-PDA at various temperatures. The DA solution shows

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