

A Polydiacetylene Supramolecular System that Displays Reversible Thermochromism

Cheol Hee Lee,¹ Jong Seung Kim,² Sun Young Park,² Dong June Ahn,³ and Jong-Man Kim*¹

¹Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

²Department of Chemistry, Dankook University, Seoul 140-714, Korea

³Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Korea

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A reversible blue-to-red color transition of polydiacetylene supramolecules derived from an oligoethylene glycol-bridged bisdiacetylene was observed upon thermal stress.

Polydiacetylenes (PDAs) are very intriguing materials in terms of their method of preparation and output signals associated with the conjugated ene-yne backbones.¹⁻⁵ Unlike most conjugated polymers, PDAs are readily prepared by irradiation (UV- or gamma-ray) of closely packed diacetylene supramolecules. Since no chemical initiators or catalysts are required for the polymerization process, the polymers are generally not contaminated with impurities and, consequently, additional purification steps are not required. Owing to their intriguing stress-induced chromic transition (blue-to-red), PDAs have been extensively investigated as potential chemosensors.⁶⁻¹²

The majority of PDA-based chemosensors reported thus far function in an irreversible fashion. Accordingly, the blue-to-red color change that takes place when an external stimulus is applied is not reversed when the external stimulus is removed. PDA systems displaying colorimetric reversibility, especially, in aqueous solution are very rare. Although colorimetric reversibility of PDA supramolecules derived from a diacetylenic phospholipid was reported,¹³ the reversible thermochromism was observed only in the narrow temperature range. Very recently, we have described a new strategy for the preparation of colorimetrically reversible PDAs.^{12b} We found strong headgroup interactions (both hydrogen-bonding and aromatic interaction) were essential for the complete colorimetric reversibility. In this communication, we report a novel colorimetrically reversible PDA supramolecular system derived from a bisdiacetylene **1** (Chart 1).

The bisdiacetylene **1** has several important features such as a hydrophilic ethylene glycol moiety, two internal amide groups, two phenyl groups, and two diacetylene units. The hydrophilic ethylene glycol group should favor water molecules and force the two diacetylene-containing hydrophobic alkyl chains to locate close together in aqueous solution. In addition, the amide groups of **1** are expected to interact with one another by hydrogen bonding. The aromatic interaction between the two phenyl groups could serve as an additional attractive force to bring

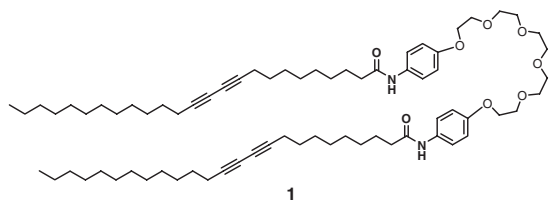


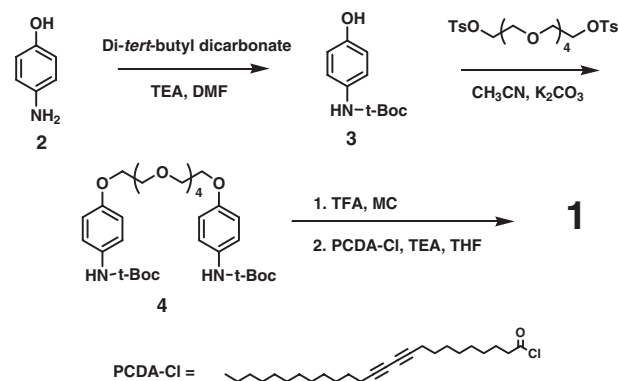
Chart 1.

the diacetylenic units close together. If the bisdiacetylene **1** can adopt a conformation as described above, facile polymerization would occur in aqueous solution and should result in polymerized diacetylene vesicles.

The synthetic procedures employed for the preparation of the bisdiacetylene **1** are shown in Scheme 1. The amine group of 4-aminophenol (**2**) was protected with a di-*tert*-butyl dicarbonate and the resulting protected aminophenol **3** was treated with pentaethylene glycol di(*p*-toluenesulfonate) to yield the oligoethylene glycol **4**. The desired bisdiacetylene **1** was readily prepared by removal of the protecting group followed by coupling with 10,12-pentacosadiynoyl chloride (PCDA-Cl).

Having prepared the desired bisdiacetylene **1**, next phase of current investigation focused on the preparation of PDA supramolecules in aqueous solution. For this purpose, a probe-sonication method was employed. Briefly, the bisdiacetylene monomer **1** was dissolved in a small amount of DMF (ca. 100 μ L) and the clear solution was added to a hot deionized water to make a 1 mM of dispersed monomer suspension. The resultant suspension was probe-sonicated for 10 min, filtered, and kept in a refrigerator for overnight to stabilize the self-assembled diacetylene vesicles. Photopolymerization of the suspension with 254-nm-UV light (1 mW/cm²) for 15 min afforded a blue-colored PDA solution. Efficient formation of PDAs and polymer particles was confirmed by visible absorption spectroscopy, color change, and scanning electron microscopic (SEM) images (see Supporting Information).¹⁴

In order to investigate the reversibility of colorimetric transition, a solution of the PDA particles were gradually heated to 95 °C while monitoring color changes by using UV-vis spectroscopy (Figure 1). At 20 °C, the PDA solution shows the typical blue color corresponding to a visible absorption maximum wavelength at 630 nm. When the temperature is raised from 20 to 95 °C, the absorption maximum of the solution undergoes a



Scheme 1. Preparation of the bisdiacetylene monomer **1**.