A Polydiacetylene Supramolecular System that Displays Reversible Thermochromism

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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 supramoleular 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 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.

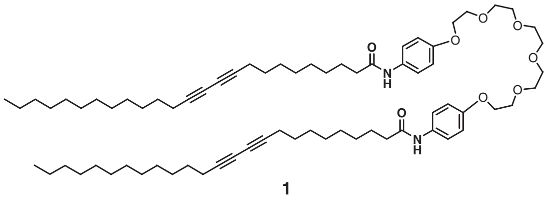

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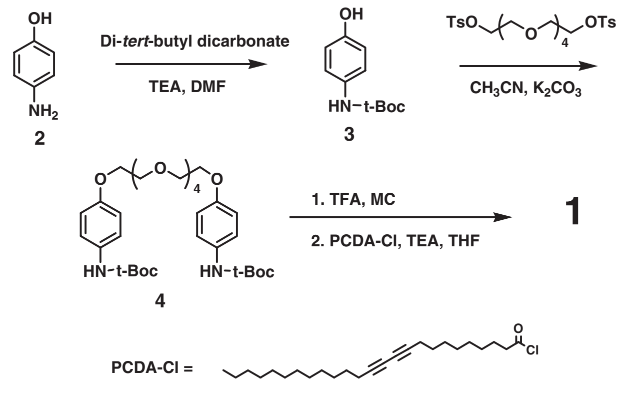
Chart 1.

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 µL) 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/cm^2) 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**.

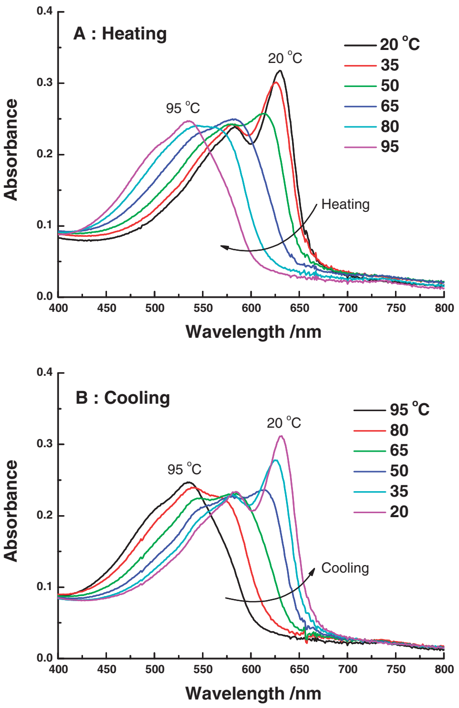


Figure 1. Visible spectroscopic monitoring of the bisdiacetylene **1**-derived PDA solution upon heating and cooling process.

gradual blue shift which plateaus at 540 nm. Upon cooling to 20 °C, the absorption maximum shifts back to 630 nm and the original intensity is recovered. The complete, thermally promoted colorimetric reversibility of this system was demonstrated by repeating the thermal cycles (see Supporting Information).

The reversible thermochromism observed with the PDA vesicles derived from **1** is very intriguing. The complete recovery of initial absorption at 630 nm after cooling the heat-treated solution (to near boiling temperature of water) indicates that very strong headgroup interactions exist. The internal amide groups should play a significant role for the colorimetric reversibility of the supramolecules as demonstrated by other systems previously reported. Thus, the strong hydrogen bonds among the amide groups should help the recovery of initial molecular orientation of PDAs after the thermal cycle. Of particular interest regarding the structure of bisdiacetylene **1** is the oligoethylene glycol linker. As explained in the introductory part, the hydrophilic nature of the ethylene glycol group would make the bisdiacetylene monomer **1** amphiphilic and should help vesicle formation in aqueous solution. In addition, the ethylene glycol linker would serve as a "holder" for the headgroups and help recovery of the original position of the headgroups after thermal cycles. Presumably by the ethylene glycol linker, the PDA supramolecules display colorimetric reversibility in the wide range of absorption spectra (λ_{max}: between 540 and 630 nm). Another feature of the spectra shown in Figure 1 is the absence of isobestic points during the heating and cooling process. Most of colorimetrically irreversible PDAs display isosbestic points in the absorption spectra during the thermal cycle. The gradual shift of absorption maxima without isosbestic points observed with PDA supramolecules derived from **1** confirms that numerous intermediate states exist during the cycle. It also indicates that the intermediate purple-colored state is not the simple combination of blue- and red-colored vesicles. It rather suggests that the effective conjugation length of the individual PDA vesicle gradually decreases. This observation is very important for the understanding of the mechanism of PDA thermochromism. The detailed investigation on the color-changing mechanism is under current investigation.

In summary, we have developed a reversible thermochromic PDA supramolecular system. The PDA solution derived from oligoethylene glycol-linked bisdiacetylene monomer **1** displayed complete reversibility in the colorimetric transition during the thermal cycle. Considering the significance of the colorimetrically reversible PDAs in the field of chemosensors, the studies discussed above should be useful in the design of new reversible PDA supramolecules.

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References and Notes

1 Reviews on polydiacetylene chemosensors: a) S. Okada, S. Peng, W. Spevak, D. Charych, *Acc. Chem. Res.* **1998**, *31*, 229. b) R. Jelinek, *Drug Dev. Res.* **2000**, *50*, 497.
2 Y. Okawa, M. Aono, *Nature* **2001**, *409*, 683.
3 Y. Lu, Y. Yang, A. Sellinger, M. Lu, J. Huang, H. Fan, R. Haddad, G. Lopez, A. R. Burns, D. Y. Sasaki, J. Shelnutt, J. Brinker, *Nature* **2001**, *410*, 913.
4 H. Bader, H. J. Ringsdorf, *Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 1623.
5 G. Wegner, *Macromol. Chem.* **1972**, *154*, 35.
6 D. H. Charych, J. O. Nagy, W. Spevak, M. D. Bednarski, *Science* **1993**, *261*, 585.
7 J.-M. Kim, S. K. Chae, Y. B. Lee, J.-S. Lee, G. S. Lee, T.-Y. Kim, D. J. Ahn, *Chem. Lett.* **2006**, *35*, 560.
8 Z. Orynbayeva, S. Kolusheva, E. Livneh, A. Lichtenshtein, I. Nathan, R. Jelinek, *Angew. Chem., Int. Ed.* **2005**, *44*, 1092.
9 G. Ma, Q. Cheng, *Langmuir* **2005**, *21*, 6123.
10 C. Wang, Z. Ma, *Anal. Bioanal. Chem.* **2005**, *382*, 1708.
11 J. Song, J. S. Cisar, C. R. Bertozzi, *J. Am. Chem. Soc.* **2004**, *126*, 8459.
12 a) J. Yoon, S. K. Chae, J.-M. Kim, *J. Am. Chem. Soc.* **2007**, *129*, 3038. b) J.-M. Kim, J.-S. Lee, H. Choi, D. Sohn, D. J. Ahn, *Macromolecules* **2005**, *38*, 9366. c) J.-M. Kim, J.-S. Lee, J.-S. Lee, S.-Y. Woo, D. J. Ahn, *Macromol. Chem. Phys.* **2005**, *206*, 2299.
13 A. Singh, R. B. Thompson, J. M. Schnur, *J. Am. Chem. Soc.* **1986**, *108*, 2785.
14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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