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# Rational Design of Supramolecular Conjugated Polymers Displaying Unusual Colorimetric Stability upon Thermal Stress**

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The colorimetric stability upon thermal stress of a series of conjugated polymer supramolecules prepared from 10,12-docosadiyndioic acid (DCDDA)-derived diacetylene monomers has been explored. Polydiacetylenes obtained from DCDDA-bis-mBzA **3**, containing *m*-carboxyphenylanilido groups at the both ends of the monomer, were observed to be highly colorimetrically stable upon thermal stimulation. The blue color of a solution containing these polydiacetylene vesicles remains unchanged even when the vesicles were subjected to boiling water. The unusual colorimetric stability is further demonstrated by the observation that blue color persists until vesicles in ethylene glycol are heated to 140 °C. The nature of this unusual thermal stability was elucidated by using polydiacetylene supramolecules, prepared from analogs of DCDDA-bis-mBzA **3**. The presence of internal amide groups as well as aromatic interactions was found to be essential for the high colorimetric stability of the polydiacetylene supramolecules.

## 1. Introduction

Owing to their extensively delocalized π-network and conformational restrictions, conjugated polymers have gained enormous attention as novel functional materials.[1] Especially interesting are stimulus-induced changes that take place in their electronic absorption and emission properties, which have been elegantly applied to the design of efficient chemo/biosensors.[2] A variety of conjugated polymers such as polythiophene, polyaniline, polypyrrole, polyphenylene, poly(phenylene ethynylene), polyacetylene, and polydiacetylene have been investigated as sensing matrices.[2] Among the conjugated polymers reported to date, polydiacetylenes (PDAs) are unique in several regards.[3–22] First, these polymers can be prepared from supramoleculary assembled crystalline or semi-crystalline states of diacetylene monomers. Conventional solution-based chemical approaches typically employed for the preparation of conjugated polymers do not yield PDAs efficiently. Second, PDAs are produced by UV or γ-irradiation of self-assembled diacetylenes without the need for chemical initiators or catalysts. Thus, the resulting polymers are not contaminated with unwanted by-products. Third, PDAs are readily prepared in aqueous solution in the form of nanostructured liposomes, vesicles and wires, which enables them to be employed as matrices for biosensing. Finally, as portrayed in Figure 1, nanostructured PDAs undergo a blue ($\lambda_{max}$: ~640 nm) to red ($\lambda_{max}$: ~550 nm) color change in response to heat (thermochromism), organic solvents (solvatochromism), mechanical stress (mechanochromism), and ligand-receptor interactions (affinochromism).[23–33]

Although significant efforts have been given to the issue,[34–36] the exact mechanism of the blue-to-red color transition is still not fully understood. The results of recent studies

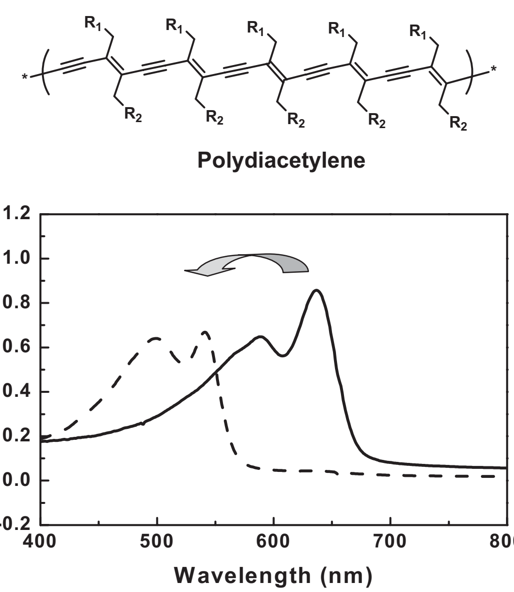


**Figure 1.** Structure of a polydiacetylene and the typical visible absorption spectral changes upon environmental stimulation.

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