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-docosa-diyniodioic acid (DCDDDA)-derived diacetylene monomers has been explored. Polydiacetylenes obtained from DCDDDA-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 DCDDDA-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), polyaacetylene, 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 supramolecularly 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 (λ<sub>max</sub>: ∼640 nm) to red (λ<sub>max</sub>: ∼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.
with urethane substituted polydiacetylenes, however, strongly suggest that the release of mechanical strain, developed on the side chains during polymerization, is the main factor responsible for the color transition. The release of sidechain strain induces a partial distortion of the conjugated π-orbital arrays, leading to the shortening of effective π-conjugation length. Our recent observations with a carboxyphenylamido-substituted diacetylene monomer, PCDA-mBzA 1 provide further support for this proposal.\[^{37}\]

During the course of investigations aimed at developing colorimetrically reversible polydiacetylene supramolecules, we found that strong headgroup interactions in the PDAs are required in order to bring about complete colorimetric reversibility during repeated heating-cooling cycles.\[^{37}\] In addition, we observed that strong headgroup interactions make the PDA supramolecules more stable to thermal stimulation. In this article, as part of our ongoing efforts for the development of PDA-based functional materials,\[^{37–41}\] we present the results of a systematic study of highly colorimetrically stable PDA supramolecules. The majority of PDA supramolecules reported to date begin to undergo blue-to-red color transitions at or below 70 °C and reach a maximum change (mostly red color) at ca. 90 °C. In contrast, the blue color of the polydiacetylene supramolecules, designed, prepared and studied in this effort, is maintained even under boiling water conditions and begins to change at 150 °C in ethylene glycol. The present findings enable the rational design of colorimetric sensor materials which operate at high temperatures, thus significantly expanding the colorimetric temperature window of PDA sensor systems.

In order to investigate structure-colorimetric stability relationships in PDAs, a series of disubstituted diacetylenic monomers 3–7 was designed employing 10,12-docosadiynedioic acid (DCDDA) (2) as a template molecule (Fig. 2). The PDA derived from bolaamphiphilic diacetylene monomer DCDDA-bis-mBzA 3 was prepared to probe colorimetric stability and to compare it with that of a PDA from the single headgroup diacetylene monomer PCDA-mBzA 1. The ester group containing diacetylene monomer DCDDA-bis-mCPE 4 was employed to gain information about the role played by amide hydrogen bonding interactions in PDAs. The effect of aromatic interactions on the colorimetric stability of PDAs was probed with polymers derived from the aminobutyric acid-derived diacetylene monomer DCDDA-bis-ABU 5. The PDA arising from the naphthoic acid-diacylene monomer DCDDA-bis-NPA 6 was studied to gain information about how extended aromatic interactions govern colorimetric properties. The mono-substituted diacetylene DCDDA-mono-mBzA 7 was selected to determine if unsymmetric headgroups in PDAs have an effect on colorimetric stability.

2. Results

2.1. Preparation of Diacetylene Monomers and Polydiacetylene Supramolecules

The diacetylenic lipid monomers 3–7 used in this study were readily synthesized in one step by coupling diacid chloride form or N-hydroxysuccinic ester (for the preparation of 5) of DCDDA 2 with corresponding amino- or hydroxy-substituted carboxylic acids. For example, treatment of the diacid chloride form of DCDDA 2 with 3-aminobenzoic acid in THF-pyridine gave the diacetylene monomer DCDDA-bis-mBzA 3. The product precipitates when the reaction mixture is poured into ice water. By using similar approaches, monomers 4–7 were prepared.

Routine procedures were used to transform the diacetylene lipid monomers 3–7 to polydiacetylenes in aqueous solution. Briefly, the diacetylene lipid was dissolved in a minimum amount of DMSO and the solution was injected into deionized water. Following probe-sonication for 15 min, the monomer suspension was filtered with a syringe filter (0.8 μm) to remove...