

Rational Design and in-Situ FTIR Analyses of Colorimetrically Reversible Polydiacetylene Supramolecules

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Received July 16, 2005; Revised Manuscript Received September 1, 2005

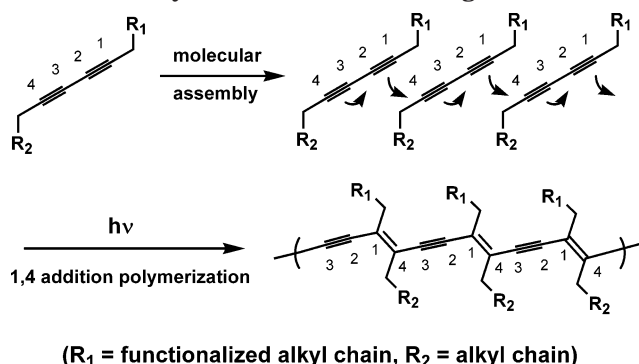
ABSTRACT: The colorimetric reversibility of polydiacetylene supramolecules, derived from a variety of functionalized diacetylenic lipids, has been subjected to detailed investigation. In an earlier effort, it was shown that polydiacetylene vesicles prepared from PCDA-*m*BzA **1**, bearing terminal *m*-carboxyphenyl-amido groups, display complete reversibility upon thermal stimulation [*J. Am. Chem. Soc.* **2003**, *125*, 8976]. The origin and nature of reversible thermochromism in these systems have been elucidated in-situ in the current studies by using polydiacetylene supramolecules, prepared from analogues of PCDA-*m*BzA **1**. Issues related to the effects of (1) internal amide groups, (2) headgroup aromatic interactions, (3) lengths of the hydrophobic alkyl chains, and (4) terminal carboxylic groups on the colorimetric reversibility of the polydiacetylene supramolecules have been probed. The results demonstrate that well-developed hydrogen-bonding and aromatic interactions between headgroups are essential for complete recovery of the length of the conjugated π -electron chain following thermal stimulus. The results of this comprehensive investigation allow for the first time the rational design of reversible colorimetric sensors based on polydiacetylene supramolecules.

Introduction

The development of efficient chemosensors based on conjugated polymers continues to be topic of great interest in both fundamental and applied research areas.¹ Conjugated polymer systems are highly attractive because changes in their absorption, emission, and redox properties are sensitive functions of environmental perturbations. A major advantage of using conjugated polymer-based chemosensors, in comparison to conventional sensors based on small molecules, is found in the potential for signal amplification when subjected to external stimuli. As a result, a wide variety of conjugated polymers, including polythiophenes,^{2–5} polyanilines,^{6–8} polypyrroles,⁹ polyphenylenes,¹⁰ and poly(phenylene ethynyls),^{11–14} polyacetylenes,¹⁵ and polydiacetylenes,^{16–37} have been investigated as sensing matrices.

Among the conjugated polymers reported to date, polydiacetylene (PDA)-based chemosensors are unique in terms of method of preparation, molecular structure, and output signal. Unlike other conjugated polymers, functionalized polydiacetylenes are prepared by using photopolymerization of self-assembled diacetylene monomers (Scheme 1). Closely packed and properly ordered diacetylene lipids undergo polymerization via 1,4-addition reaction to form alternating ene-yne polymer chains upon irradiation with 254 nm light (in the case of thin films/vesicle solutions) or with γ -irradiation (in the case of solid powders). Polydiacetylenes, generated

Scheme 1. Schematic Representation of Polymerization of Assembled Functional Diacetylenes by Irradiation with UV Light



under optimized photochemical conditions, color intense blue. In general, nanostructured polydiacetylenes investigated for use as potential chemosensors are prepared as vesicles in aqueous solutions,²⁵ Langmuir–Blodgett (LB)/Langmuir–Schaefer (LS) films,²⁸ or immobilized vesicles^{38–40} on solid supports.

The unique property of nanostructured polydiacetylenes that leads to their application as sensing elements is the occurrence of a color change from blue to red that takes place in response to a variety of environmental perturbations such as temperature, pH, and ligand–receptor interactions.^{16–33} Polydiacetylene films and vesicles, functionalized with carbohydrates, have proven to be effective biosensors for the detection of the influenza virus,²⁸ cholera toxin,²² and *E. coli*.³³ Colorimetric detection of glucose, based on ligand-induced conformational changes of hexokinase immobilized on a polydiacetylene monolayer, stands as another elegant application of polydiacetylenes biosensing.¹⁸ A system for selective detection of metal ions, formed by embedding an ionophore into the polydiacetylene liposome,

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