

Conjugated Polymer-Embedded Thermochromic Strip Sensors with a Tunable Colorimetric Response

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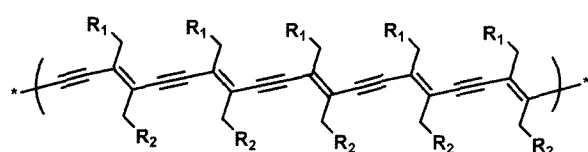
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Introduction

Polydiacetylenes (PDAs), conjugated polymers, which have alternating ene-yne backbone structures, have several very intriguing properties.¹⁻⁹ First, these materials are produced by radiation (UV or γ -ray)-induced polymerization of molecularly-assembled diacetylene (DA) monomers without the need for chemical initiators or catalysts. Second, these polymers generally have an intense blue color corresponding to maximum absorption wavelengths of *ca.* 640 nm. Lastly, the blue-colored PDAs undergo color transitions to form a red phase in response to several types of environmental stimulations such as heat (thermochromism), solvent (solvatochromism), mechanical stress (mechanochromism), and molecular recognition (affinochromism).¹⁰⁻¹⁸



Polydiacetylene

PDAs have been prepared in the form of nano/micro particles in aqueous solvent,¹³ thin molecular layers on solid substrates,¹⁰ nanotubes/nanowires,^{19,20} bulk powders¹ as well as silica composites³ and electrospun microfibers.²¹ Recently, we reported a new approach for creation of PDA supramolecules in polymer matrices.²² A flexible PDA strip sensor was readily obtained by employing a simple mixing and drying procedure. Drying of a suspension containing PDA vesicles and poly(vinyl alcohol) (PVA) in a Petri dish

afforded a thin polymer film, which undergoes a blue-to-red color transition promoted by thermal stress. Thus, the blue-colored PVA film at 25 °C becomes purple at 60 °C and eventually changes to red above 70 °C. An interesting issue with regard to these flexible PDA strip sensors is whether the color changing temperature of films of this type can be controlled by employing different types of DA monomers. If so, the colorimetric temperature window of PDA can be significantly expanded and manipulated. As part of our continuing efforts in this area aimed at the development of PDA-based functional materials,²¹⁻²⁸ we have uncovered a strategy of rationally designing thermochromic strip sensors with tunable colorimetric responses.

The five structurally different diacetylene monomers, shown in Figure 1, were selected for the purpose of making colorimetrically responsive strip sensors. In our earlier studies with DA supramolecules, we observed that strong head-group interactions in vesicles causes the resulting PDAs to be colorimetrically more stable upon thermal stimulation.²⁹ As a result, the bolamphiphilic DA monomer, DCDDA-bis-mBzA **1** that has four hydrogen-bondable groups (two amides and two carboxylic acids) and two phenyl groups is expected to produce PDAs with enhanced thermal stability. The 3-aminobenzoic acid-derived DA PCDA-mBzA **2** should enable us to test the influence of a single head group, compared with DCDDA-bis-mBzA **1**, on the colorimetric stability.

The next system should enable us to probe the effects of aromatic interactions on colorimetric stability. Compared with PCDA-mBzA **2**, the aminobutyric acid-derived PCDA-ABA **3** has a similar distance between the amide and the terminal carboxylic groups but it does not contain a phenyl ring. The DA monomer PCDA-EDEA **4** has an internal

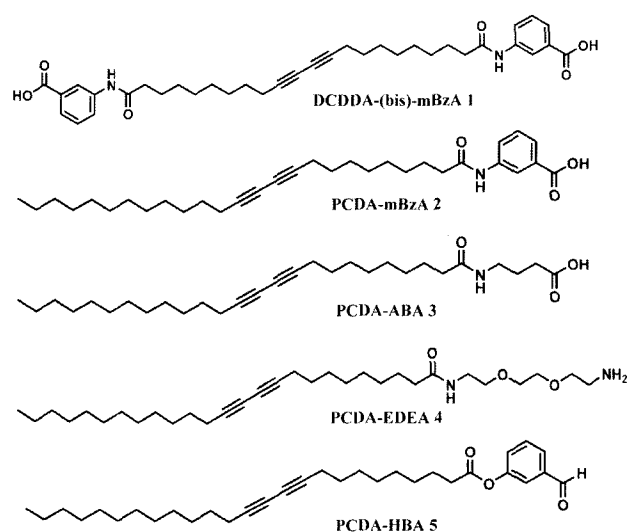


Figure 1. Structures of DA monomers investigated in this study.

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