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Patterned Color and Fluorescent Images with Polydiacetylene Supramolecules Embedded in Poly(vinyl alcohol) Films**

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Poly(vinyl alcohol) (PVA) films embedded with functional polydiacetylene (PDA) are efficiently prepared for color and fluorescence imaging. Intensely blue films are obtained by mixing and drying solutions containing PDA vesicles and PVA. A blue-to-red color transition is observed upon heating the polymer films. In addition, selective UV irradiation (through a photomask) of PVA films containing diacetylene monomer results in the generation of micropatterned color (without heating) and both color and fluorescent images (after heating the films at 120 °C for 10 s). Patterned two-color (blue and red) images in the polymer film are readily obtained by a sequential process of photomasked irradiation, heating, and unmasked irradiation.

1. Introduction

The generation of patterned functional images in polymer films is of great technological importance in fundamental and applied research areas. Since the first report of the "precursor approach" by Kim et al. for fabricating patterned fluorescent images in a polymer film,[1] the strategy, which allows development of micrometer-sized patterned functional images without employing wet developing processes, has been actively investigated by many researchers.[2] The key concept of the precursor approach is to induce a fluorescence change (either intensity or wavelength) of the precursor molecules in the UV-exposed areas. The fluorescence of the precursor molecules has been manipulated by the following photoinduced processes: i) acid-catalyzed removal of protecting groups;[1,2a–c,2j,2k] ii) keto–enol tautomerization;[2d,2f] iii) oxidation of main-chain[2h] or side-chain fluorophores;[2i] and iv) radical generation.[2e]

Polydiacetylenes (PDAs) are π-conjugated polymers that have alternating double- and triple-bond groups in the main polymer chain.[3] PDAs are unique in terms of their method of preparation, their molecular structure, and the output signal associated with their color transitions. Unlike other conjugated polymers, functionalized PDAs are prepared by irradiation of self-assembled diacetylene monomers with UV light (for thin films/vesicle solutions) or γ-rays (for solid powders). If PDAs are prepared under optimal conditions, they have an intense blue color with a maximum absorption wavelength at ca. 640 nm. In addition, the blue-colored PDAs undergo a color shift to a red phase (ca. 550 nm maximum absorption wavelength) upon environmental stimulation. Owing to their intriguing stress-induced chromic transition (blue-to-red) and nonlinear optical properties, PDAs have been extensively investigated as potential chemosensors and photonic materials.[3–10]

Another important feature of PDAs that has not gained much attention compared to the colorimetric transition is their *fluorescence*. PDAs are non-fluorescent in the "blue phase" and fluorescent in "red phase".[11] The stress-induced fluorescence change of PDA was reported only recently by our group[12] and others.[13] Since blue-colored, non-fluorescent PDAs can be readily prepared by UV irradiation, we hypothesized that selective irradiation of a diacetylene assembly using a photomask would generate a patterned, blue-colored image in the exposed areas. Furthermore, heating the blue-colored PDA film would induce a blue-to-red color transition with simultaneous appearance of a fluorescence signal. Accordingly, the generation of both color and fluorescence images would be possible using this method. As color and fluorescence images could be obtained only by a sequential irradiation and heating process, no wet development process would be required. As part of an ongoing program of research in the area of patterned functional imaging using precursor molecules[1,2a–c] and PDAs,[12,14] we report here a new methodology for constructing patterned color and fluorescent images using PDA supramolecular systems in polymer films. For this purpose, we used poly(vinyl alcohol) (PVA) as a host molecule. The use of PVA as the matrix polymer has several advantages that derive from i) its hydrophilic nature, which allows the incorporation of a variety of aqueous-based guest molecules; ii) its ready formulation as a hydrogel film; iii) its water solubility, leading to environmental friendliness; and iv) its inertness towards guest molecules.

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