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RESEARCH ARTICLE

Fluorescence Switch in Red-Phase Polydiacetylene Films and Vesicles Upon Thermal Cycles

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The switch phenomena of thermochromism of red-phase polymerized PCDA (10,12-pentacosadiynoic acid) Langmuir-Schaefer (LS) films and vesicles were investigated *in situ* during repeated heating and cooling processes between 25 °C and 70 °C. During repeated thermal cycles, the solid-supported LS films exhibited switch phenomena in both the visible and fluorescent spectra, that is, the colorimetric response (CR) of the PCDA LS films was ca. 80% at 70 °C but is ca. 50∼60% at 25 °C with an increase of fluorescent intensity in the cooling process and a decrease in the heating process. On the other hand, the PCDA vesicles exhibited such phenomenon only in the fluorescent spectra, that is, the CR of the PCDA vesicles was constant as ca. 100% after being stable red form with the same trend in the fluorescent intensity. The changes in molecular configuration revealed by *in situ* Fourier transform infrared (FTIR) were in good agreement with the trend of fluorescence emission upon repeated thermal stimuli rather than that of visible absorption.

Keywords: Polydiacetylenes, Photopolymerization, Thermochromism, Fluorescence Switch.

1. INTRODUCTION

π-Conjugated polymers have been applied to organic light emitting diodes (OLED), organic field effect transistors (OFET), photovoltaic cells, sensors, electrochromic devices, etc.[1–7] Polydiacetylenes (PDAs) are a class of linear conjugated polymers with alternating triple and double bonds in the yne-ene motif. PDAs are usually synthesized by topochemical polymerization.[8–11] The resulting polymers display interesting spectral features, from the initial metastable blue form to a stable red form[12–17] upon different environmental stimuli, such as mechanical stress,[18–21] heat,[22–25] and ligand and receptor interactions.[26–30] In general, the color transition involves a significant absorption shift from the low to high energy bands of the visible spectrum. In addition, the blue form is non-fluorescent, whereas the red form is fluorescent, indicating that the fluorescence intensity is a sensitive measure of the color transition. This color transition is also associated with other properties, such as third-order nonlinear susceptibility[31] and unique photoconduction properties.[32] It is known that molecular conformational change, such as side chain orientation and ordering, induces different backbone conformations, which alter the electronic states and corresponding optical absorption.[23,33] Thus far, many studies on polydiaceylenes focused only on the color change from blue to red as well as fluorescence change upon a single thermal stimulus. However, there are no reports of the red form experiencing periodic thermal cycles. This study focused on thermochromism of the red form of polydiacetylene films and vesicles to examine the correlation of the fluorescent intensity to repeated thermal stimuli. The changes in molecular configuration observed by the *in situ* FTIR also correlated with the switch phenomena.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Polymerized LS Films

PCDA (10,12-pentacosadiynoic acid) monomers were dissolved in chloroform at a concentration of 1 mM. The solution was spread on the air/water interface of a Langmuir trough. The assembled PCDA monomers were ordered and compressed by the barrier. The ordered multilayers of PCDA monomers were irradiated with 254 nm UV light for 40 s, and the polymerized PCDA layers were transferred once to hydrophobic glass substrates by using the horizontal touch method (Langmuir-Schaefer method).

2.2. Preparation of Polymerized PCDA Vesicles

The drop-injection method was used to prepare PCDA vesicles. The PCDA monomers were dissolved in

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