



Chromatic reversibility of multilayered polydiacetylene cast film



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ABSTRACT

The cast film of polydiacetylene and PVA on a glass surface was fabricated to demonstrate a very fast and reversible chromatic response with respect to change in temperature. The *N*-[2-(2-hydroxyethoxy)ethyl]pentacosanoic acid was sonicated in PVA solution. This solution was dried at room temperature for 3 days and the cast film was formed as multilayered structure. The UV irradiation led to *in situ* polymerization. The layered structures were confirmed by XRD data. The regularly layered polymeric cast film showed a very fast and reversible transition from blue to red. These results would be attributed to the well-arranged multilayer structure and hydrogen bonding.

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Introduction

The irreversibility of chromic response in polydiacetylene (PDA) films and vesicles was widely recognized with slow relaxation time. The fabrication of PDA films for use in any sensible devices necessarily requires increased rate of resetting of molecular states in layered structure. The chromatic response of PDA has been studied for sensing external stimuli, such as temperature [1], pH [2], mechanical stress [3], and solvents [4]. Although there are some advantages of PDA systems in direct color observation with naked eyes, the delayed change of chromatic response may not present the current state of change and thus it is necessary to explore new materials exhibiting instantaneous response of forward and backward color change.

Traditionally, the PDA systems were synthesized with two neighboring acetylenes by UV irradiation to polymerize via 1,4-polymerization. The conjugated structure of alternative arrangement of triple and double bonds in polymer backbone usually shows a blue color at room temperature. In general, the blue color undergoes a red shift by an external stimulus. The chromatic shift is believed to be due to the structural rearrangement by the external stimuli, which might disturb the electronic conjugation length of unsaturated bond [5,6]. Therefore, it is important to have a structural stability of conjugation length of polymerized diacetylene group, which could be achieved by diverse methods,

for example formation of monolayers [7], multilayers [8], particles [9], vesicles [10], immobilization on paper [11], and crystalline solids [12,13]. Unfortunately, the chromatic states of specific structures are extremely persistent against any stimuli, and the appearance and disappearance of color are not reversible except for only a few PDA systems [5,6].

A multilayered cast film, which was fabricated with a vesicle solution, was reported earlier [14,15]. The cast film was fabricated by drying a vesicle solution at a very slow pace under atmospheric pressure at room temperature with consequent formation of well-arranged multilayered molecular structure. Generally, proteins or hydrophilic polymers could stay in the hydrophilic portion of the multilayered cast film.

In this paper, we attempt to control the structures of chromatic states stabilized by the neighboring functional group in layered structure of PVA composite. A slight modification of a chromatic structure by a chemical or physical force may present the color shift, and the removal of external force may rapidly and reversibly recover the original structure [16–28]. We synthesized a 10,12-pentacosadiynoic acid (PCDA) derivative, which has a hydroxyl functional group, and formed a vesicle structure by sonication. Thus, it is proposed that the chromatic change in the film spread with the layered and hydrogen-bonded structure may be immediately reversed in response to temperature cycle. We tried to investigate the relationship of the structure of diacetylene system with the reversibility of the color transition. Therefore we investigate the effect of the formed structure by the different processing method to the reversibility of the color transition.

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Experimental

Materials and instrument

The 10,12-pentacosadiynoic acid (PCDA), PVA (M_w 89,000–98,000, 99+% hydrolyzed), *N*-hydroxysuccinimide, *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide and 2-(2-aminoethoxy)ethanol were purchased from Aldrich. Both the chemicals were guaranteed reagents and used as purchased without further purification. All other chemicals were of analytical grade and the solvents were of HPLC quality. Deionized pure water was obtained by reverse osmosis followed by ion exchange and filtration. ^1H NMR spectra were obtained from a Bruker DRX 300 spectrometer (Germany). A Cole-Parmer 4710 250 W sonicator was used for sonication to form the vesicle suspension. The vesicle size was measured by dynamic light scattering (DLS) on an ELSZ-2 instrument (Photal Otsuka Electronics, Japan) equipped with a laser diode. Transmission electron microscopy (TEM) images were obtained by a LEO-912 OMEGA instrument (Carl Zeiss, Germany). X-ray diffraction data was obtained by D8 Discover with GADDS (Bruker). The differential scanning calorimetry (DSC) studies were performed using a Scinco DSC N-650 differential scanning calorimeter under nitrogen atmosphere. All the samples (~ 10 mg) were stored within sealed aluminium DSC pans.

Synthesis of *N*-[2-(2-hydroxyethoxy)ethyl]pentacosano-10,12-dynamide (HEEPCDA)

The HEEPCDA was synthesized using PCDA as a starting material as reported previously [29]. Typically, PCDA (3.75 g, 10.0 mmol) was reacted with *N*-hydroxysuccinimide (1.50 g, 13.0 mmol) and 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (2.88 g, 15.0 mmol) to synthesize PCDA-NHS in 20 mL of dichloromethane at room temperature for 3 h. Dichloromethane was evaporated under vacuum, and purification of the residue was conducted by extraction with ethyl acetate. PCDA-NHS (3.91 g, 8.29 mmol) was obtained as a white solid (yield: 82.9%). Subsequently, PCDA-NHS (2.36 g, 5.00 mmol) in 50 mL of dichloromethane was added drop wise to 2-(2-aminoethoxy)ethanol (1.58 g, 15.0 mmol) in 100 mL of dichloromethane to synthesize HEEPCDA. The reaction was continued for 4 h at room temperature. The precipitate was filtered out and

dichloromethane solvent in the residual filtrate was evaporated under vacuum. The product was extracted from the residue, and the solution was washed with brine 3 times. The purification of the product was conducted by recrystallization with dichloromethane. Apparently, HEEPCDA (1.43 g, 3.10 mmol) was obtained as a white solid (yield: 62.0%).

NMR (CDCl_3): 0.87 (t, 3H), 1.29 (s, 26H), 1.43–1.53 (m, 6H), 2.23 (m, 6H), 3.42 (m, 4H), 3.53 (m, 2H), 3.68 (m, 2H), 4.59 (s, 1H), 6.82 (s, 1H).

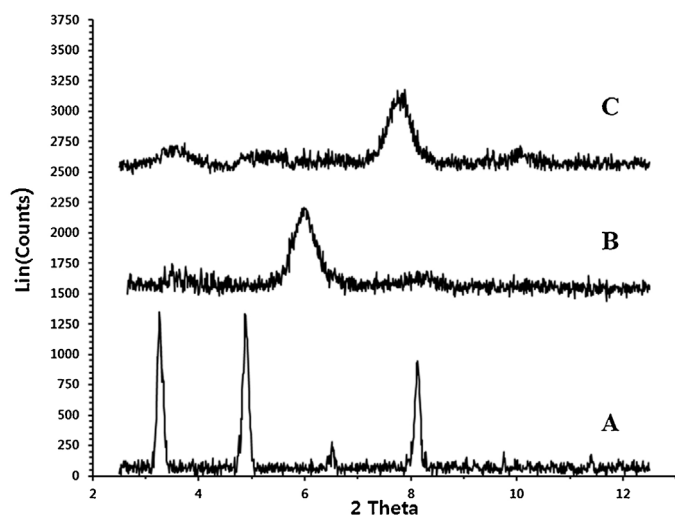
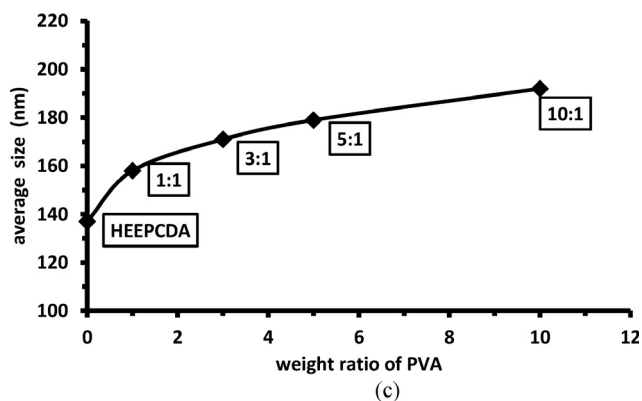
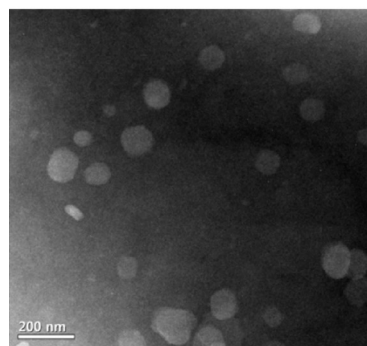
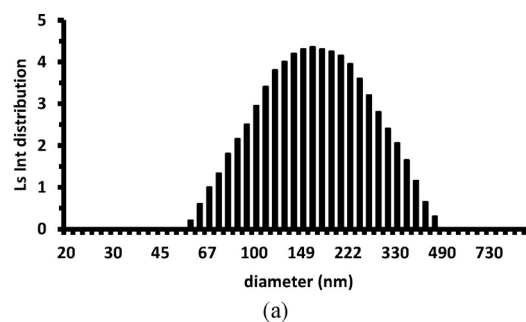
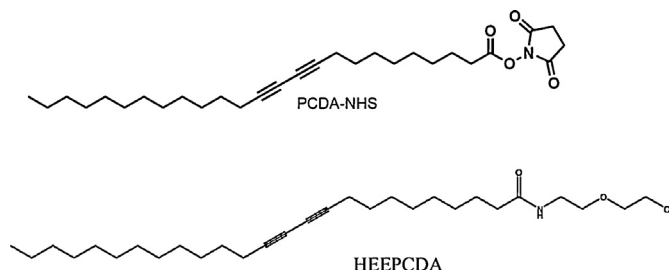


Fig. 1. XRD's of the composite film formed with PVA and HEEPCDA by different methods. (PVA:HEEPCDA = 1:1).

Fig. 2. The diameter distribution of the HEEPCDA vesicle. (a) DLS result (3:1 = PVA:HEEPCDA), (b) TEM image (3:1 = PVA:HEEPCDA), (c) the average size of HEEPCDA vesicle depending on the weight ratio of PVA obtained by DLS.

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