Polydiacetylene Supramolecules Embedded in PVA Film for Strip-type Chemosensors

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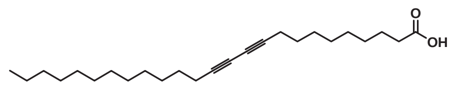
Blue-to-red color change of poly(vinyl alcohol) (PVA) films embedded with functional polydiacetylene supramolecules was observed by thermal stress or specific molecular recognition.

Recently, creation or embedment of supramolecular structures, nanoparticles, micro/nano-patterns in polymer films has gained much attention due to the intriguing properties that result from combining created/embedded materials and polymer matrices.[1,2] Films formed from this combination have many applications in optoelectronics,[3] imaging materials,[4] and sensor fabrication.[5] Among the polymer matrices explored thus far, poly(vinyl alcohol) (PVA) has become one of the most frequently used host molecules. The use of PVAs as matrix polymers has several advantages that derive from its (1) hydrophilic nature that allows incorporation of a variety of aqueous-based guest molecules, (2) ready formulation as hydrogel films, (3) water solubility leading to environmental friendliness, and (4) inertness to guest molecules.

Polydiacetylenes (PDAs) are π-conjugated polymers that have alternating double and triple bond groups in the main polymer chain. Due to the blue-to-red color transition that takes place in PDAs upon various environmental perturbations, these substances have been extensively investigated as potential sensor materials.[6,7] The majority of PDA-based sensors investigated thus far are prepared as vesicles in aqueous solutions,[7a] and Langmuir–Blodgett (LB)/Langmuir–Schaefer (LS) films.[7d] As part of an ongoing program in the area of polydiacetylenes,[7a–7c] we have developed a new methodology for constructing polydiacetylene supramolecular systems in polymer films. The method enables facile fabrication of rigorously blue-colored PVA films embedded with polydiacetylene vesicles. There is no restriction on the types of functional group that are present in the PDAs since the PDA-embedded PVAs are prepared by simple mixing of the two solutions followed by a drying process. In addition, the new approach allows manipulation of PVA film thickness so that vivid color change of PDAs in the films can be readily observed visually, a critical disadvantage of LB/LS film-based PDA chemosensors. The PDA-embedded PVA systems should be superior to PDA vesicle solutions in terms of long-term stability owing to the fact that the latter often precipitate from solution during lengthy storage periods. Finally, the method yields flexible PVA films, which can be used as strip-type (or patch-type) sensors.

Initial phase of current investigation focused on the preparation of PVA film embedded with polydiacetylene supramolecules. For this purpose, diacetylene monomer 10,12-pentacosadiynoic acid (PCDA, GFS Chemicals) having a carboxylic headgroup was selected (Scheme 1).

Embedment of PDA supramolecules in PVA films was carried out by using a mixing-drying process. A diacetylene vesicle solution (ca. 1 mM) prepared with PCDA was irradiated with 254 nm UV light to induce polymerization. The resultant blue-colored solution containing PDA vesicles was mixed with an aqueous 10 wt % PVA solution (1:1, vol %), then casted in a Petri dish and dried at 30 °C for 2 days (or at room temperature for 5 days). The blue-colored film was peeled from the dish. In Figure 1 is shown an example of a typical blue-colored, transparent PDA-embedded PVA film (thickness: ca. 180 µm) formed in this manner. The PDA-embedded PVA films were found to be very stable and could be kept for at least several months at room temperature without losing their properties.



Scheme 1.

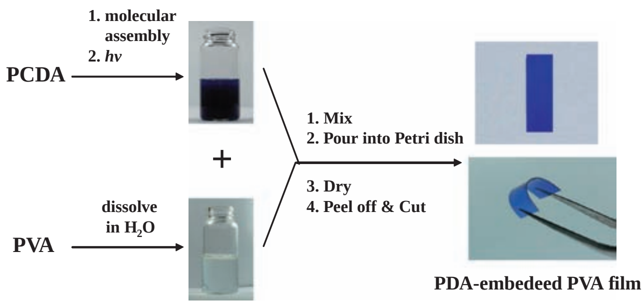


Figure 1. Fabrication of polydiacetylene-embedded PVA film.

The stress-induced color-changing properties of the PVA films embedded with PDA vesicles were investigated in the next phase of our studies. For this purpose a PDA-embedded PVA film was heated to study the thermochromic behavior of a PDA-embedded PVA film. As demonstrated by the results shown in Figure 2, the film undergoes a blue-to-red color transition in response to thermal stress. The blue-colored PVA film at 25 °C becomes purple at 80 °C and eventually changes to red above 100 °C. The heat-induced color change was found to be an irreversible process. The mixing and drying process used to construct the PDA embedded PVA film did not impose sufficient thermal stress to promote a premature color transition. This is very important observation because the derived films need to be in a "blue-phase" for their use as sensors.

The final phase of the current study probed the application of PDA-embedded PVA films to strip-type chemosensor for signaling molecular recognition events. PCDA is known to yield stable polymer vesicles in which the carboxylic headgroups form intermolecular hydrogen-bonding networks. Recently, we demon-

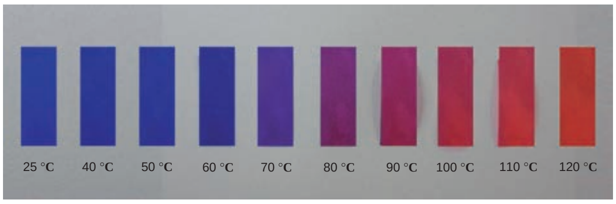


Figure 2. Photographs of the polydiacetylene-embedded PVA film during heating processes.

strated that this headgroup hydrogen-bonding network could be disrupted by α-cyclodextrin due to the formation of inclusion complex, and this disruption promotes a blue-to-red color transition of the PDA.[8] We were curious to determine if this phenomenon takes place in PDA-embedded PVA films. Accordingly, a polymerized PCDA-embedded film was prepared. A minor adjustment was made to enhance the stability of PVA film and to create pores in the polymer film which would facilitate absorption of receptor molecules from the solution. A solution of self-assembled PCDA monomer vesicles (ca. 1 mM) was mixed with a 5 wt % PVA solution (1:1 v/v). To the mixture was added silica gel (ca. 60–200 µm diameter) to make a 10 wt % silica suspension. The resulting mixture was poured in a Petri dish and placed in an oven (30 °C) for 24 h. The dried and flexible film (ca. 560 µm thickness) was irradiated with 254 nm UV light (1 mW/cm^2) for 10 min. Incubation of PDA-embedded PVA films prepared with no silica particles in CD solutions resulted in dissolution of PVA films. However, PVA-silica composite films were found to be stable during incubation and prolonged exposure (>7 days) to aqueous solutions presumably due to cross-linking between silica particles and PVAs.

The resulting blue-colored film was incubated in aqueous α-, β-, or γ-cyclodextrin (CD) solution (10 mM each). After standing for 1 h at 30 °C, the color of each of the PVA films was determined. Figure 3a contains photographs of the CD incubated PVA films. It is clear that α-CD promotes a dramatic change in the color of the film and that almost no color change is promoted by β- or γ-CD. These observations are in good agreement with those arising from evaluating the effects of the CDs on PDA solutions (Figure 3b). The degree of red color promoted was found to be dependent on the concentration of α-CD (Figure 3c).[9] Thus, PVA films embedded with PDA vesicles not only respond colorimetrically to the stress imposed by specific receptor recognition, they also provide concentration dependent profiles of the recognition process.

In summary, the studies discussed above demonstrate that PDA-embedded polymer films can be readily obtained by drying polydiacetylene-containing PVA solutions. The blue-colored thin polymer films formed in this manner undergo the typical PDA blue-to-red transition upon thermal stress. In addition, α-cyclodextrin promotes the blue-to-red color change of a PDA-embedded PVA film, formed from a carboxy-terminated diacetylene monomer. The methods uncovered in this effort establish the foundation for the development of new polydiacetylene-embedded strip sensors ("litmus-type").

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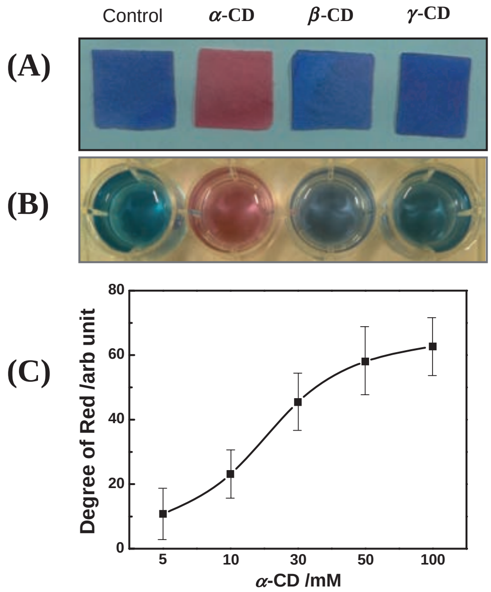

Figure 3. (A): Photographs of polydiacetylene-embedded PVA films in the presence of CDs (10 mM each), (B): Photographs of polymerized PCDA solutions in the presence of CDs (10 mM each), (C): Degree of red as a function of concentration of α-CD.

References and Notes

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9 The quantitative data of red-color intensity in the film carried out for the concentration-dependent profiles were analyzed using an AnalySIS ProII (SIS, Germany). The data were obtained with five independent experiments.

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