Cyclodextrin-induced Color Changes in Polymerized Diacetylene Langmuir-Schaefer Films

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We have observed the first example of a cyclodextrin-induced color change of polymerized diacetylene film sensor. The PDA film, prepared from a diacetylene monomer containing a terminal anilide moiety was found to preferentially interact with α-cyclodextrin causing a color transition which is both time and concentration dependent.

Since the pioneering discovery of blue-to-red color transitions induced by specific ligand-receptor interactions in polymerized diacetylenes (PDAs),[1] the development of efficient sensory systems based on nanostructured PDAs has gained much attention in both fundamental and applied research areas.[2–4]

Most of the PDA sensors developed to date have utilized specific interactions between analytes which are large, protein sized or have depended upon conformational changes of proteins. As part of our continuing efforts aimed at developing color/fluorescence changing polymers,[5–7] we have recently studied cyclodextrin-induced color transitions of PDA Langmuir-Schaefer films. Cyclodextrins are relatively small molecules, compared to proteins, and are well known for their ability to form inclusion complexes with a variety of substrates.[8] In addition, different binding specificities of the α, β, and γ cyclodextrins make these cyclic carbohydrates attractive model systems for studying ligand-receptor interactions. Accordingly, a system in which cyclodextrins cause perturbation of the polymer backbone and thereby bring about color changes of matrix PDAs, would be useful in developing a better understanding and design of PDA-based chemosensors for the detection of biologically important small and medium sized molecules.

The PDA film designed to probe the feasibility of this proposal was derived from the anilide capped, diacetylene monomer **1** (Figure 1). This substance was readily prepared by coupling 10,12-pentacosadiynoic acid chloride with aniline.[9] The PDA film was then prepared by a modified LB technique in which a chloroform solution containing 1 mM of **1** was spread onto the air/water interface of a KSV Langmuir trough containing deionized water as the subphase. Following equilibration at 25 °C for 20 min to allow chloroform to evaporate, the lipid film was over-compressed to form multilayered liquid-condensed phase and polymerized by irradiation with 254 nm UV light of the intensity of 1 mW/cm^2 for 45 s to give a blue-colored film. The film was then transferred to hydrophobized glass slides precoated with octadecyltriethoxysilane by use of the horizontal-touch Langmuir-Schaefer method.

The PDA film was incubated in cuvettes containing appropriate concentrations of cyclic and linear carbohydrates in [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid] (HEPES) buffer (5 mM, pH = 8.0). Each film was removed from the cuvette and color changes were monitored by the UV-visible spectroscopy. The initial effort focused on determining the effect of α-cyclodextrin on possible color transitions of the PDA film since this cyclic polysaccharide was expected to form an inclusion complex with the terminal anilide moieties.

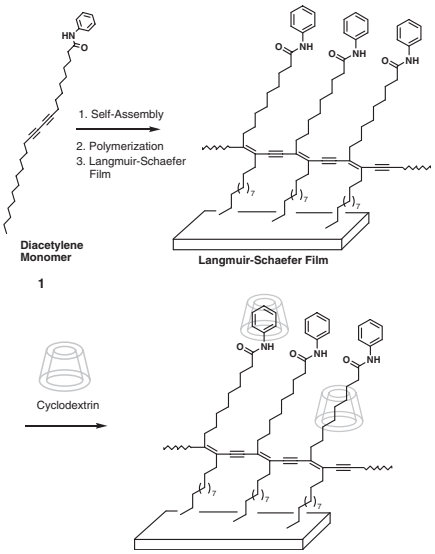

Figure 1. The structure of anilide containing diacetylene monomer **1** and a schematic representation of interaction between cyclodextrin and PDA film sensor.

As seen by viewing the UV-visible spectral changes shown in Figure 2(A), α-cyclodextrin solutions (20 mM, HEPES buffer) promoted a time dependent decrease of the absorption band at 640 nm and a simultaneous increase at 550. In order to quantify this colorimetric response (CR), the well-defined equation[2] $CR = (PB_0\text{-}PB_f)/PB_0 \times 100\%$ (PB_0 and PB_f are percent blue before and after the color transition, $PB = A_{640\,nm}/[A_{640\,nm} + A_{550\,nm}]$) was used. The CR values of the PDA film caused by α-cyclodextrin were calculated to be 21, 38, and 91% for t = 60, 90, and 180 min, respectively. In addition, the concentration dependencies of the induced color changes were also determined. As seen by viewing the plot shown in Figure 2(B), the times required to reach the maximum color changes decrease as the concentrations of α-cyclodextrin increases.

In order to investigate the carbohydrate selectivity of the

induced color changes, PDA films were incubated for 2 h with varying concentrations of linear and cyclic polysaccharides, including β- and γ-cyclodextrins,[10] and monosaccharides including glucose and maltotriose (Figure 3). Interestingly, the color transition of the PDA film is not triggered by γ-cyclodextrin. This observation demonstrates that the sensor capability of this film is preferential to α-cyclodextrin. It is hard to draw a definitive conclusion with the result from β-cyclodextrin due to its low solubility.

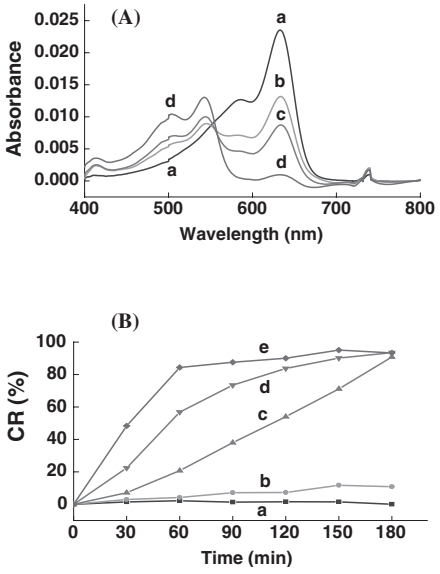

Figure 2. (A): Visible spectroscopic monitoring of the PDA film with α-cyclodextrin (20 mM) in HEPES buffer solutions (5 mM, pH = 8.0, 25 °C) for a (0), b (60), c (90), and d (180 min), respectively (B): Plot of the colorimetric response (CR) of the PDA film after incubation in HEPES buffer with various concentrations of α-cyclodextrin: a (1), b (10), c (20), d (30), and e (40 mM), respectively. In all case, the PDA films were removed from the cuvettes after the designated time periods and spectra were recorded immediately with the films.

In order to demonstrate that the color changes described above are due to inclusion complex formation, the PDA film was incubated for 4 h in a buffer solution containing α-cyclodextrin and 40 mM 4-nitrophenol (4-NP), a substance known to form tight binding complexes with this cyclic oligosaccharide. While 4-nitropheol itself had no effect on the wavelength maximum of the PDA film, this phenol significantly inhibits the α-cyclodextrin-induced color transition (Figure 3(d)).

In summary, we have observed the first example of a cyclodextrin-induced color changes of polymerized diacetylene film sensor. The PDA film, prepared from a diacetylene monomer containing a terminal anilide moiety was found to preferentially interact with α-cyclodextrin causing a color transition which is both time and concentration dependent. Other linear and cyclic polysaccharides were found to be ineffective in their ability to promote a color transition in this PDA film. Inhibition of the color change in the presence of 4-nitrophenol shows that the wavelength maximum shift is due to the formation of an inclusion complex.

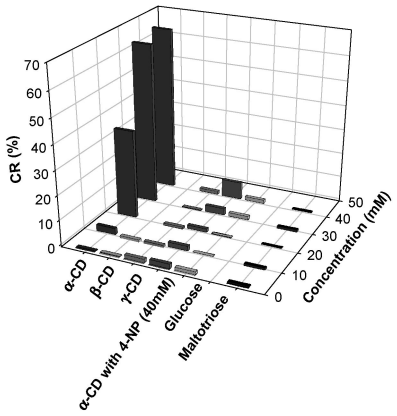

Figure 3. The colorimetric response (CR) of the PDA film after 2 h incubation with various concentrations of the specified carbohydrates in HEPES buffer (5 mM, pH = 8.0, 25 °C).

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9 Mp 55-56 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.87$ (m, 3H), 1.06-1.80 (m, 35H), 2.06-2.40 (m, 6H), 7.02-7.58 (m, 5H); ^{13}C NMR: δ = 14.1, 19.1, 22.6, 25.5, 28.2-29.6, 31.8, 65.2, 119.8, 124.2, 129.0, 138.0, 171.5.
10 Because of its low solubility, experiments using concentrations of β-cyclodextrin higher than 10 mM were not used.