

Colorimetric Reversibility of Polydiacetylene Supramolecules Having Enhanced Hydrogen-Bonding under Thermal and pH Stimuli

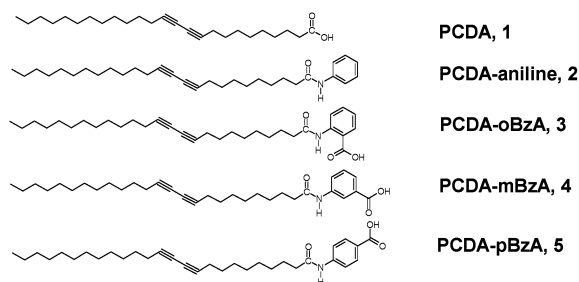
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Self-assembled polydiacetylene supramolecules^{1–3} in the form of Langmuir–Schaefer (LS) or Langmuir–Blodgett (LB) films and liposomes are attractive owing to their functionalizability and applicability to colorimetric detection systems. Unique “blue-to-red” colorimetric transition of variously modified polydiacetylene supramolecules has been utilized to monitor ligand–receptor binding events involving viruses,⁴ toxins,⁵ glucose,⁶ and ionic interactions.⁷ The polydiacetylene-based chemosensors reported to date, however, function via irreversible fashion. Accordingly, once the blue-phase shifts to the red-phase upon a given external stimulus, the backward “red-to-blue” transition does not occur even though the stimulus is removed afterward from the system. To the best of our knowledge, two examples of reversible chromism of the polydiacetylene liposomes have been reported against temperature with diacetylenic double-chain phosphatidylcholines⁸ and against ionic binding with hydrazide-modified single-chain diacetylene lipids.⁹ In this Communication, we report the first example of both thermally stimulated and pH-stimulated reversible polydiacetylene LS films made of a novel single-chain diacetylene derivative capable of enhancing the strength of hydrogen-bonding of the resulting assemblies. The role of enhanced hydrogen-bonding is also spectroscopically analyzed *in situ*.

The strategy for the design of the reversible polydiacetylene supramolecules is as follows. It has been well known that the polymerized LB/LS films and liposomes prepared with 10,12-pentacosadiynoic acid (PCDA, **1**) do not show reversible chromism



against temperature and pH. We reasoned that the hydrogen-bonding of the carboxylic headgroups of polymerized PCDA was not strong enough for the supramolecules to maintain proper molecular organizations required for the reversible color switching. Accordingly, adding another functional group to the headgroup capable of additional hydrogen-bonding would affect the nature of overall hydrogen-bonding, thus allowing the supramolecules to be in adequate conditions for the reversible chromism. One obvious way

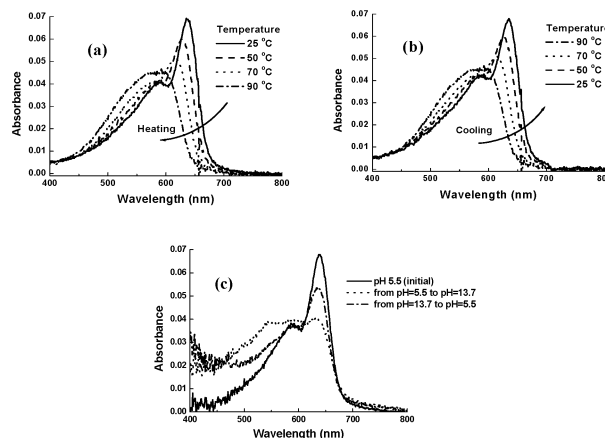


Figure 1. Reversible colorimetric transitions of LS films made from molecule **4**: as thermal stimulus was imposed (a) and removed (b), and as pH was varied (5.5 $\rightarrow$ 13.7 $\rightarrow$ 5.5) (c).

to add another functional group to PCDA is to utilize substituted anilines. Coupling of an aniline derivative with PCDA should give an amide moiety and an additional functional group, in this case, a carboxylic group in the same molecule. Both functional groups are capable of hydrogen-bonding, and the position of the terminal carboxylic group can be manipulated by selecting proper substituents. Thereby, diacetylene derivatives containing an unsubstituted anilide group **2** and carboxy-substituted (ortho-, meta-, and para-) anilide groups **3–5** were prepared. Monomeric molecules of PCDA derivatives were assembled into ordered multilayers on a Langmuir trough, polymerized by exposure to UV light (254 nm, 1 mW/cm²), and then transferred by the LS method to hydrophobized glass or CaF₂ slides. All the diacetylene derivatives except the compounds **3** and **5** were found to form stable blue-colored LS films.

As expected, the blue-colored LS film made of the molecule **2** was colorimetrically irreversible upon removal of thermal and pH stimuli after its first transition from blue to red. The purple-colored LS film prepared with ortho-substituted **3** showed no sign of reversibility. Interestingly, the LS film obtained with meta-substituted **4** was found to have a remarkable reversibility (Figure 1). At room temperature, the film prepared with **4** showed typical absorption spectra having a maximum absorption wavelength at 640 nm and another at 580 nm being relatively small but evident. During heating from room temperature to 90 °C, the maximal absorption shifted gradually downward from 640 nm and finally reached 580 nm with temperature (Figure 1a). This is quite different from the typical case of the molecule **1**, showing a simultaneous absorption increase at 550 nm with an absorption decrease at 640 nm, without having a gradual peak shift. This indicates that the average conjugation length of π electrons along the polymer

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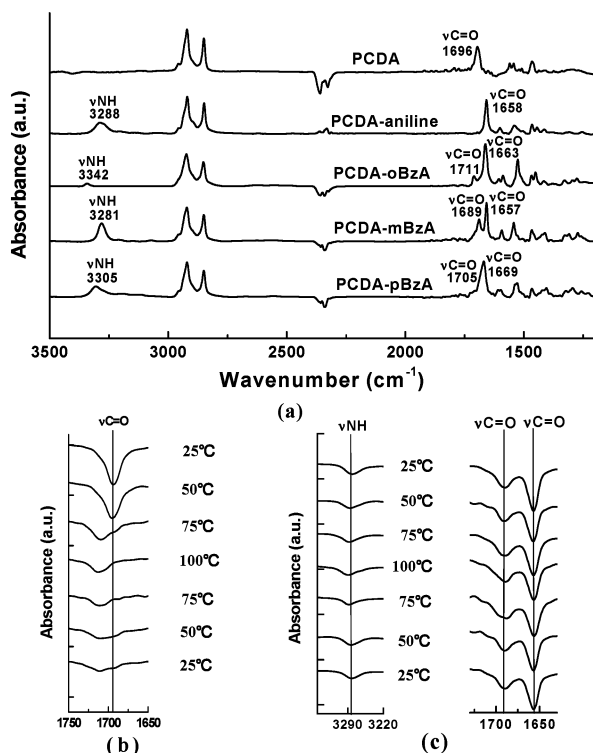


Figure 2. Transmission FTIR spectra of LS films of polymerized PCDA derivatives on CaF_2 (a), and in situ external reflection FTIR spectra of LS films of PCDA (b) and PCDA-*mBzA* (c) on hydrophobized glass.

backbone changed gradually from the initially popular 640 nm (blue phase) to 580 nm (purple phase) for the molecule **4**, unlike the abrupt change from 640 to 550 nm for the molecule **1**. During cooling to 25 °C, the maximal absorption shifted upward to 640 nm, and the original intensity was recovered (Figure 1b). Upon repeating such thermal cycles, the color of the LS films switched between blue and purple without losing the initial and final intensities at 640 and 580 nm, respectively. The LS film of para-substituted **5** was colored faint blue due to a lesser degree of topopolymerization and showed an incomplete reversibility.

The LS film of the molecule **4** also showed an interesting feature against pH change from 5.5 (Figure 1c). When the pH increased abruptly to 13.7, the film underwent a colorimetric transition. As the pH was adjusted back to 5.5, the original blue color was immediately recovered, which was not possible in other cases.

To examine the nature of hydrogen-bonding among the headgroups, transmission FTIR spectroscopic analyses were executed for the LS films of molecules **1**–**5** deposited on CaF_2 substrates (Figure 2a). While molecule **1** had a hydrogen-bonded carbonyl stretching band at 1696 cm^{-1} , molecule **2** had hydrogen-bonded amide and carbonyl stretching bands at 3288 and 1658 cm^{-1} , respectively. Molecules **3**–**5** were found to possess all three of these hydrogen-bonded bands.¹⁰ Among these molecules, molecule **4**, containing terminal *mBzA*, showed relatively stronger hydrogen-bondings for all of the three bands, as indicated by lower peak positions. When compared to molecules **1** and **2**, molecule **4** showed a higher or comparable strength both for the terminal carbonyl hydrogen-bonding (1689 cm^{-1}) and for the amide-carbonyl hydrogen-bonding (3281 and 1657 cm^{-1}), which was not the case for the other molecules. In situ FTIR analyses (Figure 2b and c) revealed detailed information on the state of headgroups upon thermal stimulus. During heating over 75 °C, the hydrogen-bonded carbonyl stretching band of molecule **1** shifted from initial 1696 to 1710 cm^{-1} , indicating reduction of its strength. However, during cooling

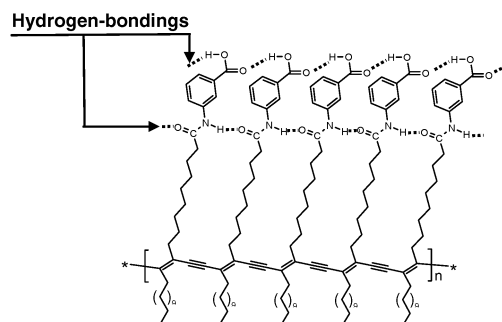


Figure 3. Schematic of enhanced hydrogen-bonding at terminal carboxyl and amide-carbonyl groups. Although only intramolecular bondings are schematically indicated, intermolecular ones are also possible.

back to 25 °C, the strength of hydrogen-bonding was not recovered. By contrast, molecule **4** maintained the initial strength of hydrogen-bondings upon the thermal cycle, as indicated by the absence of a peak shift. Hence, it seems most probable that sturdy, well-developed double hydrogen-bondings among headgroups of molecule **4** (Figure 3) provide its supramolecular film with the capability to recover its initial molecular organization, so that the average conjugation length of the π electrons returns to the initial value upon removal of external stimuli. The results on the role of enhanced hydrogen-bonding in color change should be potentially useful for designing reversible colorimetric sensors based on polydiacetylene supramolecules.

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Supporting Information Available: Experimental details on the syntheses of the diacetylene derivatives, the formation of their LS films, and the spectroscopic analyses (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Molecule **5** showed a weak shoulder at 1705 cm^{-1} due to the terminal carbonyl stretching nearly perpendicular to the electric field of the infrared beam.

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