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# Layer-by-Layer Deposition of Polydiacetylene Vesicles and Linear Poly(sulfonates)

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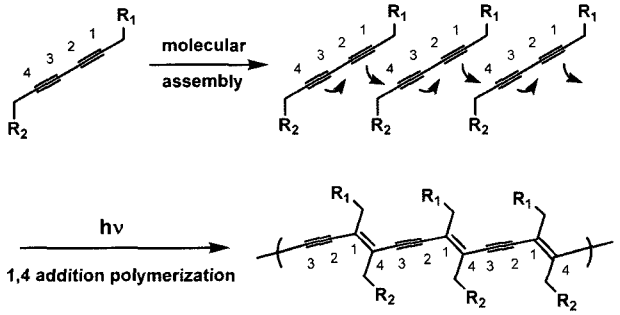
## Introduction

Fabrication of functional supramolecular structures through the self-assembly of small molecules continues to be the subject of keen interest.[1] Molecularly-assembled monomers having polymerizable units often provide additional merits to the resulting supramolecules such as enhanced stability and/or chromogenic functions. In this regard, polydiacetylene (PDA) supramolecules, uniquely prepared by UV irradiation of molecularly assembled diacetylene monomers without employing additional catalysts or initiators, are very attractive (Scheme I).[2-10] The polymer backbone of polydiacetylenes is consists of alternating ene-yne structures. Due to the intriguing stress-induced chromic transition (blue-to-red) and nonlinear optical properties, PDAs have been extensively investigated as potential chemosensors and photonic materials.[2-10]




($R_1$ = functionalized alkyl chain, $R_2$ = alkyl chain)

**Scheme I.** Schematic representation of polymerization of molecularly assembled functional diacetylenes by irradiation with UV light.

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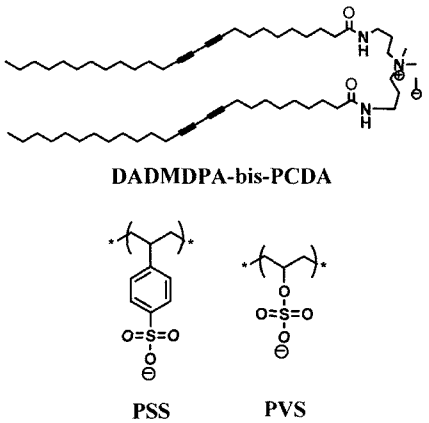
The majority of polydiacetylenes investigated for use as chemosensors have been prepared as vesicles in aqueous solutions and Langmuir-Blodgett (LB)/Langmuir-Schaefer (LS) films. Recently, we and other group reported immobilized PDA vesicles on solid supports.[8,12a,12j] During the investigation for the development of efficient PDA-based immobilized chemosensor systems, we felt that the signal intensity of PDAs would increase if the PDA vesicles could be deposited in a layer-by-layer fashion on the solid substrates. The layer-by-layer deposition method which utilizes electrostatic interaction between oppositely charged polyelectrolytes has proven to be very efficient for the construction of layered nanostructures as well as for enhancing signal intensities.[11] As part of our ongoing efforts for the development PDA-based chemosensors,[12] we now report preparation of layered PDA systems by alternative deposition of positively charged PDA vesicles and negatively charged linear polymers. The diacetylenic monomer and linear polymers investigated in this study is shown in Scheme II.

## Experimental

**Materials.** 10,12-Pentacosadiynoic acid (PCDA) was purchased from GFS chemicals. Poly(sodium styrene sulfonate, Mw=70,000) and poly(potassium vinyl sulfate, Mw=170,000) were purchased from Aldrich. The *N*-hydroxysuccinimide ester of 10,12-pentacosadiynoic acid (PCDA-NHS) were prepared as described in the literature.[12d]

**Preparation of DAMDPA-*bis*-PCDA.** A solution con-




**Scheme II.** Structures of cationic diacetylene monomer DADMDPA-*bis*-PCDA and anionic linear polymers, poly(styrenesulfonate) (PSS) and poly(vinyl sulfate) (PVS) investigated in this study.

taining 3,3'-diamino-*N*-methyldipropylamine (DAMPPA) 0.169 mL (0.5 mmol) in 1,4-dioxane (10 mL) was added dropwise to the solution containing 500 mg (1.06 mmol) of PCDA-NHS in 30 mL of 1,4-dioxane at room temperature. The resulting solution was stirred for overnight at room temperature. After concentrating *in vacuo*, the residue was redissolved in 5 mL of THF. Product was precipitated out by pouring the THF solution into excess water. Yield: 0.25 g (29%) as a white solid; mp 69 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=0.88 (t, 6H), 1.20-1.80 (m, 64H), 2.14-2.42 (m, 19H), 3.33 (q, 4H), 6.40 (s, 2H).

**Preparation of Cationic Diacetylene Monomer DADMDPA-*bis*-PCDA.** To a solution containing 0.2 g (0.232 mmol) of DAMDPA-*bis*-PCDA in 30 mL of THF was added dropwise 0.1 mL (1.624 mmol) of iodomethane and the resultant mixture was stirred for overnight at room temperature. The resulting solution was stored in refrigerator for overnight. The precipitates was filtered to give 0.12 g (52%) of the desired diacetylene monomer DADMDPA-*bis*-PCDA as a white solid; mp 103 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=0.88 (t, 6H), 1.20-1.80 (m, 64H), 2.14-2.42 (m, 16H), 3.15 (s, 6H), 3.43 (t, 4H), 3.57 (q, 4H), 7.27 (t, 2H).

**Preparation of Polymerized Diacetylene Vesicles.** The cationic monomer DADMDPA-*bis*-PCDA was dissolved in chloroform and the organic solvent was removed by purging with $N_2$ to generate a thin lipid film on the glass surface. A buffer solution (HEPES, 5 mM, pH=8.0) was added to yield a total PCDA lipid concentration of 0.5 mM. The samples were then heated at 80 °C for 15 min and probe sonicated (Fisher Sonic Dismembrator Model 550 W, 25% of the power) for 15 min. The resulting solution was filtered through a 0.8 m filter and the filtrate was cooled at 4 °C for 12 h. Polymerization was carried out at room temperature by irradiating the solutions with 254 nm UV light (1 mW/cm$^2$) for 2 min.

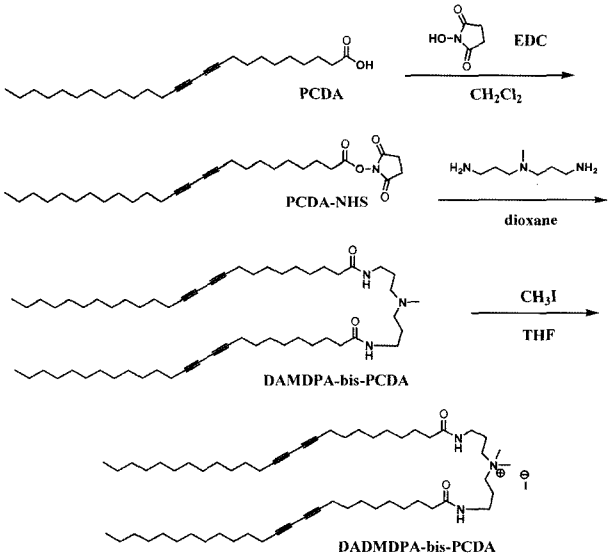
**Layer-by-Layer Deposition.** A solution containing sodium hydroxide (10 mM) in methanol (10 mL) was mixed with deionized water (90 mL). A clean glass substrate was dipped in the resulting solution and heated at 50 °C for 2 h. The substrate was then rinsed several times with deionized water. The negatively-charged glass slide prepared was immersed in a 0.5 mM DADMDPA-*bis*-PCDA vesicle solution for 5 min at room temperature and then washed with deionized water. After drying over $N_2$, the glass was then dipped into an aqueous solution (1 wt%) of negatively-charged polymers (poly(styrenesulfonate) or poly(vinyl sulfate)) for 5 min at room temperature. These procedures were repeated until the desired deposition was obtained.

**Atomic Force Microscopy (AFM).** AFM images were collected using a Multimode Nanoscope IIIa AFM (Digital Instruments, Santa Barbara, CA). AFM measurements were operated in tapping mode. Si tips had resonance frequencies between 280 and 320 kHz and an effective radius of curvature at the tip was 10 nm.

## Results and Discussion

**Synthesis of Cationic Diacetylene Monomer DADMDPA-*bis*-PCDA.** Synthetic sequences employed in the preparation of the diacetylenic monomer DADMDPA-*bis*-PCDA are shown in Scheme III. Coupling of commercially available PCDA with *N*-hydroxysuccinimide gave the activated ester PCDA-NHS. Treatment of the activated ester PCDA-NHS with DAMDPA allowed formation of the intermediate bisdiacetylenic tertiary amine DAMDPA-*bis*-PCDA. The desired cationic diacetylene monomer DADMDPA-*bis*-PCDA was readily prepared by reacting the intermediate DAMDPA-*bis*-PCDA with iodo-methane in teterahydrofuran (THF). Fortunately, the final product was precipitated out from THF solution and washing the precipitate with excess THF gave pure monomer.

**Preparation of Cationic Polydiacetylene Vesicles.** Routine procedures were used to transform the cationic diacetylene lipid monomer DADMDPA-*bis*-PCDA to polydiacetylene vesicles in aqueous solution. The monomer DADMDPA-*bis*-PCDA was dissolved in chloroform and the organic solvent was removed by purging with $N_2$ to generate a thin lipid film on the glass surface. A buffer solution (HEPES, 5 mM, pH=8.0) was added to yield a total monomer lipid concentration of 0.5 mM. The sample was then heated at 80 °C for 15 min and probe sonicated for 15 min. The resulting solution was filtered through a 0.8 $\mu$m filter and the filtrate was cooled at 4 °C for 12 h. Polymerization was carried out at room temperature by irradiating the solutions with 254 nm UV light (1 mW/cm$^2$). A typical deep blue-colored solution




**Scheme III.** Synthesis of cationic diacetylene monomer DADMDPA-*bis*-PCDA.

was obtained when a sonicated solution containing the monomeric diacetylenes was irradiated with 254 nm UV light.

Figure 1(A) shows visible spectra of a diacetylene-containing deionized solution. As can be seen from the spectra, absorption at 640 nm gradually increases with irradiation time. Irradiation for 3 min was found to be sufficient for the purpose of current investigation. Prolonged irradiation sometimes cause color change of the polymer solution.

**Layer-by-Layer Deposition.** In order to obtain layered PDA structures, a clean glass substrate was pretreated with 0.1 mM NaOH solution. The negatively charged glass substrates then were incubated in a PDA vesicle solution to immobilize the first layer of positively charged PDA vesicles. After PDA immobilization, the glass substrate was washed with deionized water. The glass substrate then was incubated in a poly(styrenesulfonate) (PSS) solution followed by washing with deionized water. Multilayered polydiacetylenes were prepared by repeating these procedures. Incubation in each solution was lasted for 5 min and the substrate was washed with deionized water for 1min before incubation in a counter ionic solution.

Figure 2(A) displays absorption spectra of a glass substrate deposited with layered PDA vesicles. It is clear that the absorbance increases as the number of deposition cycle increases. Figure 2(B) presents plots of absorbance at 636 nm as a function of a deposition cycle. It is found that PSS is superior to poly(vinyl sulfate) (PVS) as a counter anionic polymer. Control experiments without using the counter anionic polymer, PSS or PVS, confirm that these polymers are required for efficient deposition of polydiacetylene vesicles. We could not observe significant difference between using low (Mw=70,000) and high (Mw =1,000,000) molecular weight PSS in terms of deposition efficiency (data not shown).

In order to characterize surface morphology of the layer-by-layer deposited polydiacetylenes, atomic force microscopic (AFM) analysis was performed. In Figure 3 is displayed a representative AFM image of the surface after 5 deposition cycles prepared with DADMDPA-*bis*-PCDA and PSS. The image shows 50-200 nm-sized immobilized polydiacetylene vesicles.

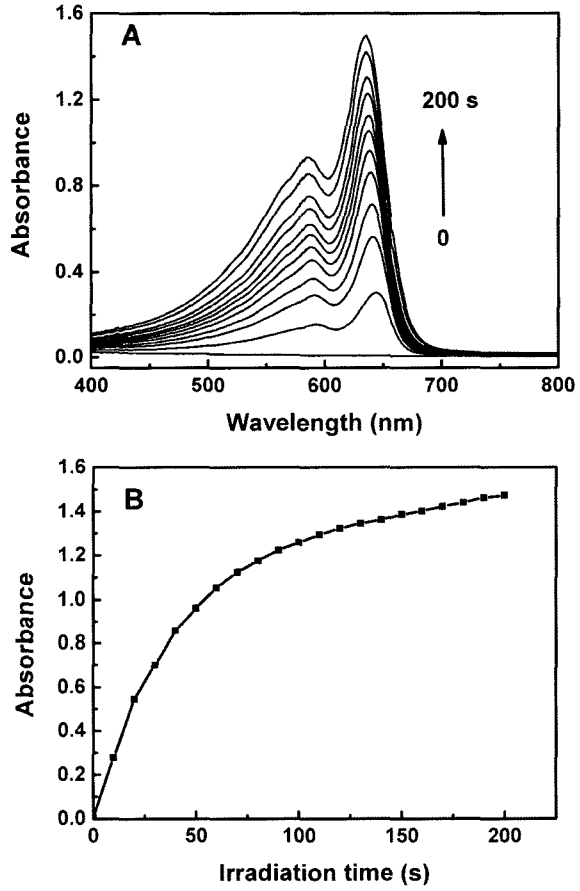



**Figure 1.** Visible absorption spectra (A) of a diacetylene solution irradiated with UV light and plots of absorption at 640 nm (B) as a function of irradiation time.

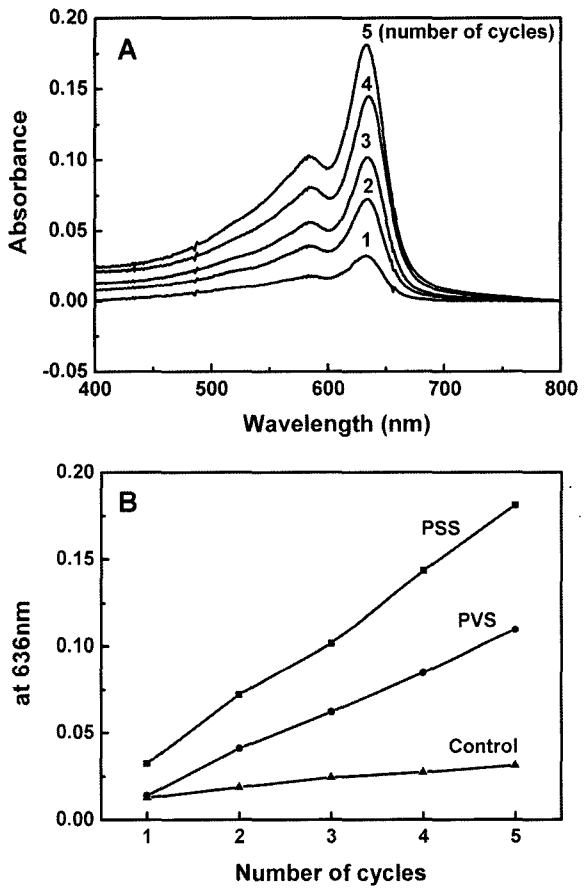



**Figure 2.** Visible spectroscopic monitoring of DADMDPA-*bis*-PCDA multi-layer deposition glass (A) and plots of absorption at 636 nm (B) as a function of the number of deposition cycle (B).

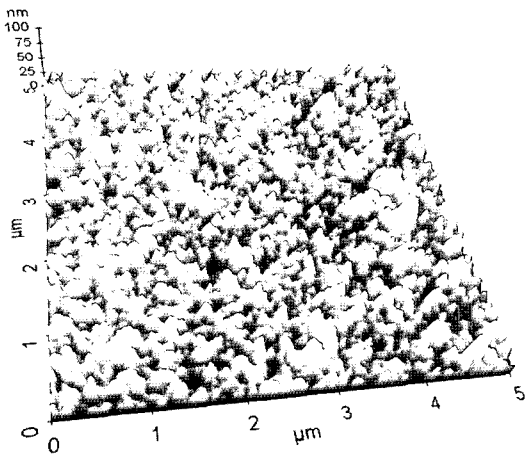



**Figure 3.** AFM image of deposited polydiacetylenes prepared with DADMDPA-*bis*-PCDA and PSS.

**Thermochromic Properties.** Final phase of current investigation focused on the thermochromism of the multilayered PDA vesicles. PDA supramolecules are well known for their color transition properties upon various environmental stimulations. Among stresses which induce blue-to-red color transition, thermal stimulation has been most extensively investigated.[2,12b] In addition, the reversibility of the color change is another issue that has gained much attention. In order to investigate the thermochromism and reversibility of the colorimetric transitions, a glass substrate coated with multi-layered PDA vesicles derived from DADMDPA-*bis*-PCDA and PSS was gradually heated to 80 °C while monitoring color changes by using UV-visible spectroscopy (Figure 4). At 20 °C, the glass substrate coated with multi-layered PDA vesicles shows the typical blue color corresponding to a visible absorption maximum wavelength at 640 nm. When the temperature is raised from 20 to 80 °C, the absorption maximum undergoes a gradual blue shift. Upon cooling to 20 °C, the absorption maximum shifts back to 640 nm. Although the absorption at 520 nm was not completely recovered, the multi-layered PDA vesicles shows almost reversible thermochromism.

The near complete reversibility could presumably be due to strong amide headgroup interactions via hydrogen bonding. In addition, the bisdiacetylenic structures restrict the mobility of the headgroups which help regain of the original conformation after removal of the thermal stress.

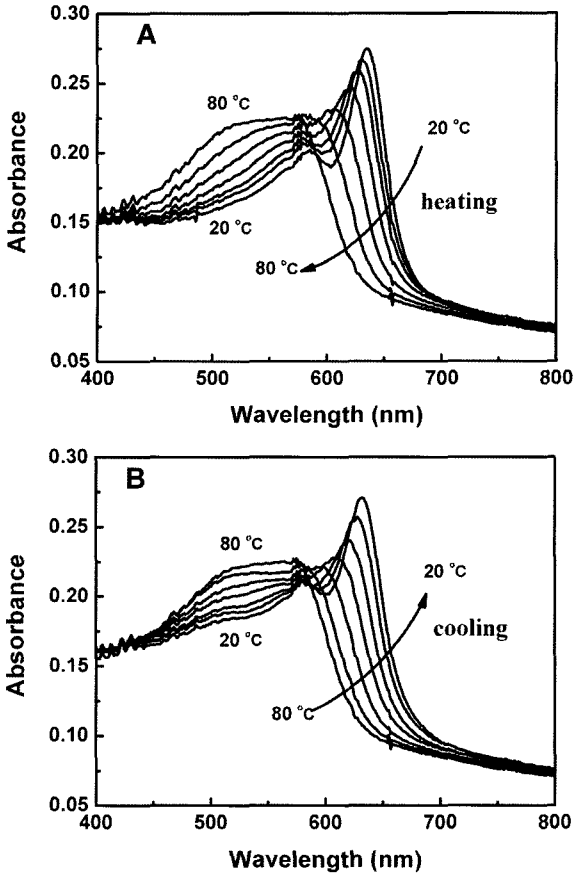
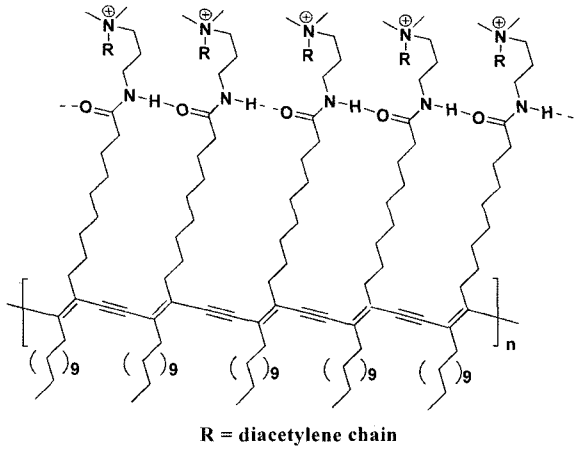



**Figure 4.** Visible spectroscopic monitoring of deposited polydiacetylenes prepared with polymerized DADMDPA-*bis*-PCDA and PSS upon heating and cooling processes.




**Scheme IV.** A schematic representation of possible headgroup interactions.

## Conclusions

We have prepared a multi-layered polydiacetylene vesicles on a glass substrate employing a layer-by-layer deposition method. A cationic bisdiacetylene monomer was readily prepared and the molecularly assembled monomers in an aqueous solution were photopolymerized to generate polymer vesicles. Layered polydiacetylenes were prepared by alternative deposition of positively charged polydiacetylene

vesicles and negatively charged linear polymers such as PSS and PVS. The method described in current investigation should be useful when increase of signal intensity of polydiacetylene-based sensor system is necessary.

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