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

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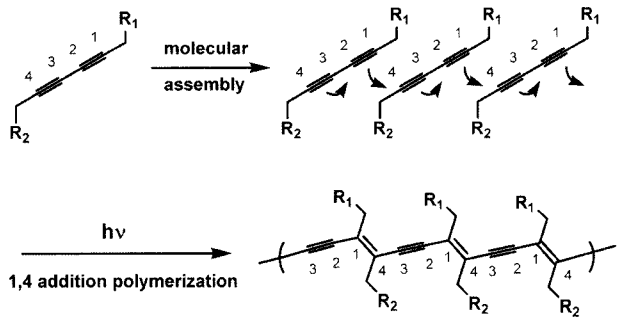
Introduction

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]

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.



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

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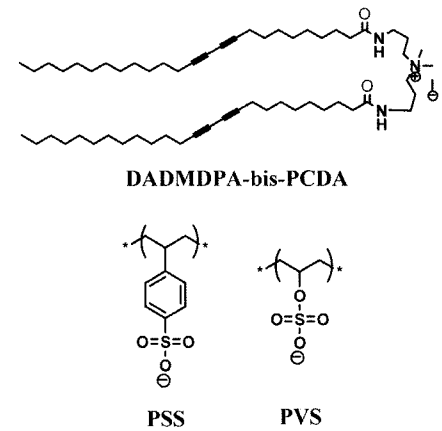
Experimental

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.