Macromolecular Research

Article

DOI 10.1007/s13233-018-6071-7

www.springer.com/13233 pISSN 1598-5032 eISSN 2092-7673

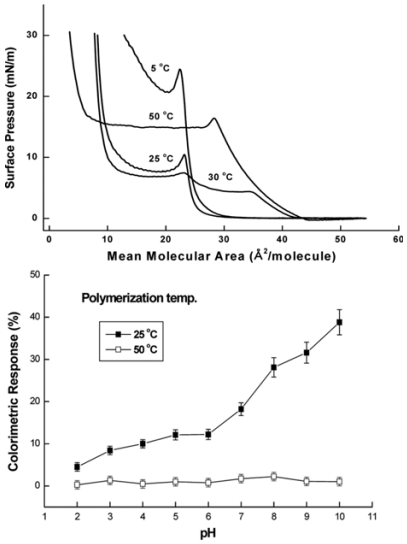
Temperature-Dependent Phase Behavior of Langmuir Films of 10,12-Pentacosadiynoic Acid at the Air/Water Interface and Its Effects on Chromatic Stability of the Polymerized Langmuir-Schaefer Films

Gil Sun Lee[1]
Sung Jun Hyun[2]
Dong June Ahn*[,2,3]

[1] Department of General Education, Kookmin University, Seoul 02707, Korea
[2] Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Korea
[3] KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Korea

Received November 29, 2017 / Revised December 29, 2017 / Accepted January 2, 2018

Abstract: The effect of temperature on the two-dimensional phase of 10,12-pentacosadiynoic acid (PCDA) Langmuir films at the air/water interface was investigated. The temperature of the Langmuir films was precisely controlled from 5 to 50 °C and their surface isotherms and *in-situ* visible absorption spectra were acquired. Depending on the temperature, the PCDA Langmuir films were found to be classified into a liquid-condensed (low temperatures, 5 and 25 °C) and a liquid-expanded phase (high temperatures, 40 and 50 °C). After polymerizing the PCDA Langmuir films with 254 nm UV light at the specific temperatures, the films were transferred to hydrophobic glass using the Langumir-Schaefer (LS) method. Upon thermal and pH stimuli, their chromatic transition characteristics were analyzed by visible spectroscopy. The liquid-condensed films were found to be more susceptible to thermal stimulus than the liquid-expanded films. The latter also showed remarkable chromatic stability against the pH in the region from 2 to 11, compared to the former. Thus, when sturdy films are required, the multilayered PCDA LS films prepared at the liquid-expanded phase are more suitable than the liquid-condensed films, and vice versa. This result is expected to be very useful for controlling the sensitivity and stability of polydiacetylene-based sensory systems simply by changing the polymerization temperature, even without synthesizing new monomers.



Keywords: polydiacetylene, polymerization temperature, chromatic stability, Langmuir films, Langmuir-Schaefer.

1. Introduction

The recent development of sensors based on polymerized molecular assemblies of diacetylene derivatives has drawn much attention due to their potential applications to inexpensive quick assays.[1-4] Polydiacetylene-based sensors need no separate transducers, and the signals are amplified within the polymer backbone containing consecutive ene-yne moieties. The apparent chromatic transition in polydiacetylenes from blue to red can be induced by a variety of external stimuli such as pH,[5-8] temperature,[9-12] solvent,[13-15] ligand-receptor interaction,[1,16-22] ammonia gas,[23] and crystal deposition.[24,25] This chromatic transition is attributed to changes in the conjugation length of π-electrons along the backbone.[14,26,27] In order to apply the polydicetylenes to sensors, it is very important to easily modulate their chromic characteristics. Previously reported methods include mainly the syntheses of new molecular structures and the compositional changes of diacetylene-rich mixtures. The molecular structural properties of the diacetylene polymer such as the distance from the backbone to the terminal head groups and the total length of the alkyl chain can modulate the chromatic susceptibility against temperature and UV light exposure.[28-32] The physical incorporation of a second component such as a ligand molecule into the diacetylene matrix destabilizes the blue phase state and thus increases the sensitivity both in the thermochromic and biochromic responses.[28,33] The biochromic response can be tuned by adjusting the compositional ratio of the incorporated ligand molecules to diacetylene molecules. It would be more plausible to discover a simpler way to modulate the chromatic characteristics without altering molecular structures or compositions. In this work, we report a new way of chromatic modulation by changing a simple processing condition such as the polymerization temperature. The temperature influences the Langmuir films of 10,12-pentacosadiynoic acid at the air/water interface to be in the liquid-condensed or in the liquid-expanded states, which in turn affects the chromatic characteristics of the subsequent Langmuir-Schaefer (LS) films deposited on solid substrates against thermal and pH stimuli. The results offer a simpler way for controlling the sensitivity and stability of polydiacetylene-based sensory systems.

Acknowledgments: This research was supported by the National Research Foundation of Korea (NRF 2017R1A2B3006770, 2017M3D1A1039421) and the Korea University Grant.

***Corresponding Author:** Dong June Ahn (ahn@korea.ac.kr)