Molecular Imaging of Thermochromic Carbohydrate-Modified Polydiacetylene Thin Films

Anna Lio,[†] Anke Reichert,[†,‡] Dong June Ahn,[§] Jon O. Nagy,[†] Miquel Salmeron,[†] and Deborah H. Charych*[,†]

Lawrence Berkeley National Laboratory, Center for Advanced Materials, Berkeley, California 94720, and Department of Chemical Engineering, Korea University, Seoul 136-701, Korea

Received April 21, 1997. In Final Form: July 18, 1997[⊗]

Polymerized thin films based on polydiacetylenes (PDAs) undergo distinct color transitions that lend themselves to applications in biosensing, surface modification, nonlinear optics, and molecular electronics. The mechanism of the thermochromic blue to red color transition of PDA thin films was investigated at the molecular level using atomic force microscopy and at the macroscopic level with visible absorption and Fourier transform infrared spectroscopy. The thermochromic transition temperature is found to be between 70 and 90 °C. At the molecular level, the ordering of the film *increases* at the thermochromic transition and remains ordered up to temperatures well above the transition (e.g., 130 °C). No evidence for previously suggested entanglement or disordering of the alkyl side chains is observed. The pendant side chains rearrange from a partially disordered configuration characteristic of the blue film, to a well-ordered close-packed hexagonal arrangement in the red form. The rearrangment of the pendant side chains is linked to the formation of the red phase PDA.

Introduction

The blue to red color transition of polydiacetylenes (PDAs) has inspired researchers for several decades.[1−5,13] These color changes occur in polydiacetylene single crystals, cast films, solutions, and Langmuir−Blodgett (LB) films. They arise from a variety of environmental perturbations including temperature (thermochromism)[3] and mechanical stress (mechanochromism).[4] We have recently demonstrated that biomimetic polydiacetylenes incorporating carbohydrate ligands change color from blue to red upon specific binding of a biological target (biochromism).[5−7] An example of such a lipid−polymer membrane film is shown in Figure 1. The films are composed of 10,12-pentacosadiynoic acid (PCA) and carbohydrate derivatives of PCA (e.g., sialic acid, SA-PCA), and prepared by the Langmuir−Schaefer (LS) technique. The molecular assembly depicted in Figure 1 was designed to mimic the spatial organization and functionalization of natural cell membranes that are similarly "sugar coated". Molecular recognition at the carbohydrate interface is reported as a color change by the conjugated polydiacetylene polymer backbone of alternating triple and double bonds.[6] The color change, typically from blue to red arises from reduction of the effective conjugated length of the polymer ene−yne backbone. Films such as that shown in Figure 1 have been used to detect the binding of influenza virus as this virus normally binds to sialic acid residues on cell surfaces.[8−10] The sialic acid diacetylenic lipid is dispersed in the "matrix" lipid of PCA.

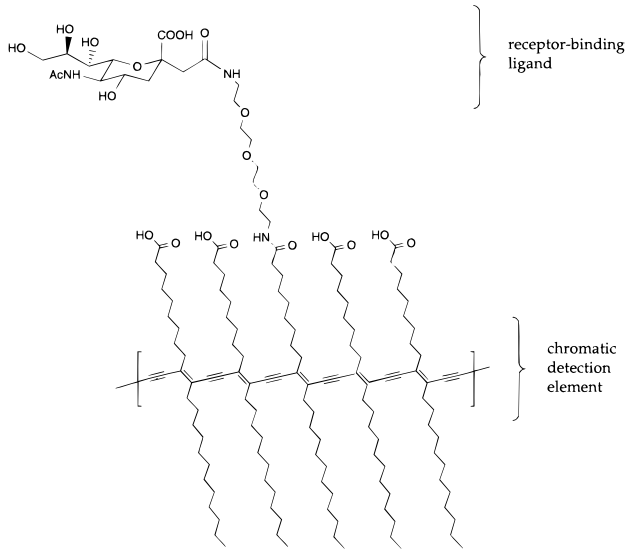

Figure 1. Schematic diagram of the carbohydrate-modified molecular assembly used for these studies. The conjugated polymer backbone of alternating double and triple bonds constitutes the chromatic detection element. The sialic acid carbohydrate is a receptor-specific ligand for influenza virus.

In order to fully exploit the use of ligand-modified polydiacetylene films as biosensors, it is necessary to develop a complete molecular-level understanding of the blue to red color transition. In the longer term, an understanding of the molecular mechanisms underlying the optical transition may lead to optimized systems that are responsive to a variety of physical phenomena, as well as chemical and biological agents. To this end, we have

* To whom correspondence should be addressed.
† Lawrence Berkeley National Laboratory.
‡ Present address: BASF-Aktiengesellschaft, Polymer Research, ZKD/B-B1, D-67056, Ludwigshafen, Germany.
§ Korea University.
⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) Bloor, D.; Chance, R. R. *Polydiacetylenes*; NATO ASI Series E; Applied Science; Martinus Nijhoff Publishers: Dordrecht, 1985.
(2) Tieke, M.; Wegner, G. In *Topics in Surface Chemistry*; Kay, E., Bagus, P. S., Eds.; Plenum Press: New York, 1978.
(3) Wenzel, M.; Atkinson, G. H. *J. Am. Chem. Soc.* **1989**, *111*, 6123.
(4) Galiotis, C.; Yong, R. J.; Batchelder, D. N. *J. Polym. Sci. Polym. Phys. Ed.* **1983**, *21*, 2483.
(5) Charych, D. H.; Nagy, J. O.; Spevak, W.; Bednarski, M. D. *Science* **1993**, *261*, 585.
(6) Reichert, A; Nagy, J. O.; Spevak, W.; Charych, D. *J. Am. Chem. Soc.* **1995**, *117*, 829.
(7) Charych, D.; Cheng, Q.; Reichert, A.; Kuziemko, G.; Stroh, M.; Nagy, J. O.; Spevak, W.; Stevens, R. C. *Chem. Biol.* **1996**, *3*, 113.
(8) White, J.; Kielian, M.; Helenius, A. *Q. Rev. Biophys.* **1983**, *16*, 151.
(9) Paulson, J. C. *The Receptors*; Conn, M., Ed.; Academic Press: New York, 1985; Vol. 2, pp 131−219.
(10) Spevak, W.; Nagy, J. O.; Charych, D. H.; Schaefer, M. E.; Gilbert, J. H.; Bednarski, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 1146.

S0743-7463(97)00406-X CCC: $14.00