

## Simple Detection of Food Spoilage Using Polydiacetylene/Poly(vinyl alcohol) Hybrid Films

Sera Park<sup>†,1</sup>, Gil Sun Lee<sup>†,2</sup>, Chunzhi Cui<sup>\*,1,3</sup>, and Dong June Ahn<sup>\*,1,4</sup>

<sup>1</sup>Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Korea

<sup>2</sup>Department of General Education, Kookmin University, Seoul 02707, Korea

<sup>3</sup>Department of Chemistry, Yanbian University, Yanji 133002, P. R. China

<sup>4</sup>KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul, 02841, Korea

Received November 24, 2015; Revised January 14, 2016; Accepted January 16, 2016

**Abstract:** Polydiacetylene (PDA)/poly (vinyl alcohol) (PVA) hybrid films are investigated for detection of ammonia gas generated by the food spoilage process. The films were obtained by mixing solutions containing diacetylene vesicles and aqueous PVA, and then drying. The films, which consist of carboxylic-acid-terminated PDA, showed a blue-to-red color transition upon reaction with ammonia gas. Through Fourier transform infrared (FTIR) analysis, we found that the observed color transition resulted from an ionic interaction between the carboxyl group of PDA and ammonia gas. In addition, patterned films were fabricated by selective UV irradiation through a photomask. Finally, the PDA/PVA hybrid films were found to show a color transition after reaction with real proteinic food at 25 °C. These results verify that the PDA/PVA hybrid films can be used for easier and more convenient real-time detection of food spoilage by the naked eye.

**Keywords:** polydiacetylene, poly(vinyl alcohol), food spoilage, ammonia detection.

### Introduction

Nitrogenous proteinic foods such as meat and fish have been described as the most perishable type of important foods. Spoilage of these foods is caused by specific pathogenic bacteria such as *Salmonella*,<sup>1-3</sup> *Escherichia coli* O157:H7,<sup>4,5</sup> and *Campylobacter*.<sup>6,7</sup> As foods are spoiled by these bacteria, the surface levels of glucose decrease significantly. It was reported that once the surface glucose has been exhausted, pathogenic bacteria metabolize secondary substrates, such as free amino acids. The utilization of free amino acids leads to an increase in the levels of ammonia<sup>8</sup> and other volatile compounds such as sulphides, indoles, and amines.<sup>9</sup>

Despite their various advantages, conventional methods for detecting food spoilage, such as culture methods,<sup>10</sup> enzyme-linked immunosorbent assays (ELISAs),<sup>11</sup> and polymerase chain reaction (PCR),<sup>12</sup> are labor-intensive, time-consuming, and lack sensitivity and specificity. To make up for these weaknesses, numerous methods for testing the freshness of foods have been developed recently, including electronic nose systems,<sup>13,14</sup> near infrared (NIR), Fourier transform infrared (FTIR) spectroscopy,<sup>15</sup> liquid chromatography-mass spectrometry (LC-MS),<sup>16</sup> gas chromatography-mass spectrometry (GC-MS),<sup>17</sup> and ion mobility spec-

trometry (IMS).<sup>18</sup> In spite of numerous efforts, food-borne human infections persist, and improved methods of testing and monitoring bacterial and parasitic contamination need to be developed.

As  $\pi$ -conjugated polymers, polydiacetylenes (PDAs) have received considerable attention owing to their optical and electrochemical properties.<sup>19,20</sup> PDA polymers are formed by the 1,4-addition reaction of self-assembled diacetylene monomers upon irradiation with UV light. The resulting PDAs have an intense blue color with a maximum absorption peak at *ca.* 640 nm and they are non-fluorescent. These polymers show color transition from blue to red, with a maximum absorption peak at *ca.* 550 nm and red fluorescence, in response to various external stimuli, such as heat,<sup>21,22</sup> pH,<sup>23</sup> solvent,<sup>24</sup> mechanical stress,<sup>25</sup> and ligand-receptor interactions.<sup>26</sup> For this reason, numerous PDA-based sensors have been developed for the detection of biological and chemical target molecules.<sup>20,27</sup>

Herein, we report the first example of a PDA sensor for real-time monitoring of the freshness of proteinic foods with naked eye by detecting ammonia gas generated by food spoilage. We chose poly(vinyl alcohol) (PVA) as a matrix polymer for the PDA sensor because of its hydrophilicity and inertness towards guest molecules, which allows the incorporation of various aqueous-based guest molecules and ensures environmental friendliness.<sup>28-30</sup>

\*Corresponding Author. E-mail: ahn@korea.ac.kr

<sup>†</sup>These authors equally contributed to this work.