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Fabrication of sensory structure based on poly (ethylene glycol)-diacrylate hydrogel embedding polydiacetylene

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Abstract−Hydrogel-based sensory structures were developed by embedding polydiacetylene supramolecules into poly-(ethylene glycol)-diacrylate (PEG-DA) to detect chemical gases and cyclodextrin and to determine pH values on the basis of a fluorescence change. We found the optimal condition for patterning-fabrication by controlling the volumetric mixture ratio of the water-soluble PEG-DA and aqueous polydiacetylene vesicle solution. Then, we determined that this hydrogel-based polydiacetylene structure optically responded selectively against vapor-phase targets: ammonia, ethanol, and aldehyde; aqueous solutions with various pH values; and cyclodextrin derivatives. These results could be extended to various label-free sensing applications of hydrogel-based chemo-biosensors.

Keywords: Hydrogel, PEG-DA, Polydiacetylene, Chemo-biosensor

INTRODUCTION

Hydrogels have been widely investigated due to their intriguing properties, namely, their hydrophilicity and biocompatibility [1,2]. They have an ability to absorb large amounts of water and have water content as a result of their three-dimensional network structure consisting of hydrophilic polymer chains. They are also responsive to various stimuli. Therefore, it is essential to fabricate patterned structures for application in biomedical or nanotechnology fields [3-6]. The photopolymerization of water-soluble polyethylene glycol (PEG) macromer, one of the hydrogels, provides stable and biocompatible gels [7-13]. A unique characteristic of PEG-diacrylate (PEG-DA) is that the photopolymerization is propagated by free radicals from the dissociation of the photoinitiator under UV irradiation of 365 nm. During the reaction, the PEG-DA prepolymer can undergo a cross-linking reaction and result in a network structure. Conjugated polydiacetylenes have attracted great interest as a component of sensors due to their bichromatic properties. These polymers are formed via a 1, 4-addition reaction upon exposure to UV light and undergo a transition from a blue, non-fluorescent form to a red, fluorescent form in response to structural changes induced by external stimuli. Therefore, functionalization of the surface of polydiacetylene with molecular receptors has been used to develop label-free biological/chemical sensors [14-25]. In this study, we combined the unique characteristics of polydiacetylene and hydrogels to fabricate new sensory structures by embedding polydiacetylene supramolecules into the PEG-DA hydrogel and realized the detection of three chemical gases (ammonia, ethanol, and formaldehyde) based on the optical and fluorescent changes of the polydiacetylene.

EXPERIMENTAL

1. Materials

PEG-DA (M_n:700), 2-hydroxy-2-methylpropiophenone as the photoinitiator, ammonia anhydrous (≥99.98%), ethanol (95%), formaldehyde solution (36.5-38%), α-cyclodextrin (≥98%), β-cyclodextrin (≥97%), and γ-cyclodextrin (≥98%) were purchased from Sigma-Aldrich. 10,12-Pentacosadiynoic acid (PCDA) and 6,8-heneicosadiynoic acid (HCDA), diacetylene derivatives, were purchased from GFS Chemicals.

2. Preparation of Diacetylene Vesicles

Standard methods were used to transform the diacetylene monomers to diacetylene vesicles in an aqueous solution [15,20]. Diacetylene monomers (PCDA and HCDA) were dissolved in chloroform and the solvent was evaporated by purging with nitrogen gas. Deionized water was then added to yield a total monomer concentration of 1 mM and the solution was hydrated at 80 °C for 15 min. The hydrated suspension was probe-sonicated (Fisher Scientific, Pittsburgh, PA, USA) for 15 min. Following sonication, the solution was filtered through a mixed cellulose ester (MCE) membrane with 0.8 μm pores to remove aggregated supramolecules and then stabilized at 4 °C overnight.

3. Fabrication of PEG-DA/Polydiacetylene Hydrogel

The diacetylene vesicle solution was polymerized by exposure to 254 nm UV light at an intensity of 1 mW/cm^2 for 10 min. The polydiacetylene vesicle solution was then mixed with the PEG-DA solution containing 2 vol% photoinitiator. The resultant solution was cast in a chamber (thickness: ca. 5 mm). Overhead projector (OHP) film was first covered on the chamber, and a soda lime glass-photomask then covered the OHP film. The solution was cross-linked by exposure to 365 nm UV light for 2 min. Finally, the pho-

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