Macromolecular Research Note

DOI 10.1007/s13233-017-5124-7 www.springer.com/13233 pISSN 1598-5032 eISSN 2092-7673

Optimal Photoluminescence Achieved by Control of Photopolymerization for Diacetylene Derivatives That Induce Reversible, Partially Reversible, and Irreversible Responses

Sang Ho Park[†,1]
Jinkyu Roh[†,1]
Dong June Ahn[*,1,2]

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

Received May 2, 2017 / Revised May 16, 2017 / Accepted May 30, 2017

1. Introduction

Special properties of conjugated polymers, such as colorimetric transition,[1] fluorescence[2,3] and electrical conduction,[4,5] have made conjugated polymers promising organic materials in a myriad of applications.[6,7] Many researchers have studied the development of chemosensors based on conjugated polymers.[8-11] Among the conjugated polymers reported to date, polydiacetylene (PDA) are unique in terms of their method of preparation and molecular structure.[10] Closely packed and properly ordered diacetylene (DA) go through polymerization *via* 1,4-addition reaction to form ene-yne polymer chains on irradiation with 254 nm UV light without the need for initiators or catalysts.[12] The reaction in the delocalized π-electron conjugation length of PDA is the main factor that imparts the blue-to-red color transition and red fluorescence emission.[13,14] Although numerous PDA structures have been prepared in deionized water, most of them undergo irreversible color transition upon stimulation.[15] In an earlier work carried out by Singh and coworkers, an aqueous suspension of the polymerized DA obtained from the bisdiacetylenic phosphorylcholine was found to undergo reversible thermochromism in the range of 10-60 °C.[16] Other researches on the properties of polydiacetylene have focused mainly on the colorimetric transition and red fluorescence at red phased PDAs.[17]

Previous observations have suggested that the conformational change at the back bone is the main factor responsible for the colorimetric transition and the number of polar head groups, which are capable of the hydrogen bonding, is closely related to reversibility.[18,19]

Red fluorescence signal emission is the key characteristic of PDA vesicles that have led to their widespread application to biological and chemical sensing and thus, we envisaged that an optimization of the emitted signal would be valuable in sensing and imaging applications. In this study, we focused on generating enhanced optical signals by the control of photopolymerization, which is yet to be investigated for derivatives of diacetylene with respect to their optical reversibility.

Acknowledgments: This work was supported by the National Research Foundation of Korea (NRF 2017R1A2B3006770, 2015M3C1A3002152), KU-KIST Graduate School of Converging Science and Technology, and a Korea University Grant.

***Corresponding Author:** Dong June Ahn (ahn@korea.ac.kr)
[†]These authors contributed equally.

2. Experimental

2.1. Materials

10,12-Pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid (TCDA) was purchased from GFS Chemicals. Aminobutric acid (ABA) and aminobenzoic acid (mBzA) modified diacetylene monomers (PCDA-ABA, TCDA-ABA, PCDA-mBzA and TCDA-mBzA) were synthesized by previously literature.[19] Dimethyl sulfoxide (DMSO) and chloroform were purchased from Sigma-Aldrich.

2.2. Preparation of PCDA and TCDA vesicles

1 mM PCDA or TCDA monomer was dissolved in chloroform. The solvent was then evaporated by purging with nitrogen gas and 20 mL of deionized water added. The solution was heated with shaking at 80 °C for 15 min and further sonicated for 15 min. The resulting suspension was filtered through a 0.45 μm filter to remove aggregates and cooled at 4 °C for 6 h.

2.3. Preparation of ABA and mBzA modified vesicles

PCDA-ABA, TCDA-ABA, PCDA-mBzA or TCDA-mBzA monomers, measured for 1 mM, were dissolved with 1 mL DMSO and filtered *via* 0.2 μm filter to remove oligomers. The solution was gradually injected in 20 mL deionized water with shaking at 80 °C for 15 min and sonicated for 15 min. The resulting solution was filtered through a 0.45 μm filter to remove aggregates and cooled at 4 °C for 6 h.

2.4. Polymerization and stimulation

The DA vesicles were polymerized under 254 nm UV light (1 mW/cm^2) for 1 min, 10 min, 1 h and 2 h. Afterwards, the thermal stimulation was carried out at 110 °C for 30 min.

2.5. Characterization

Optical property were analyzed by UV-Vis spectroscopy (8453, Agilent) and fluorescence spectroscopy (F-7000, Hitachi).

