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# ION AND TEMPERATURE SENSOR FROM POLYDIACETYLENE

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A Dissertation Submitted in Partial Fulfillment of the Requirements  
for the Degree of Doctor of Philosophy Program in Chemistry

Department of Chemistry

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พอลิไดอะเซทิลีนเป็นคอนจูเกตพอลิเมอร์ที่น่าสนใจโดยมีคุณสมบัติทางสีที่สามารถประยุกต์ใช้ในงานด้านเซ็นเซอร์ แต่ทว่าในงานวิจัยเกี่ยวกับพอลิไดอะเซทิลีนยังต้องการความเข้าใจเกี่ยวกับกลไกการเปลี่ยนแปลงสี และการพัฒนาการใช้งานให้สะดวก ในงานวิจัยนี้ประสบความสำเร็จในการเตรียมฟิล์มบางแบบหลายชั้นที่เตรียมจากพอลิเมอร์ประจุบวก ไคโตซานหรือพอลิเอทิลีนอิมมีน และพอลิเมอร์ประจุลบของ พอลิ 10,12-เพนตะโคไซด์อายโนอิก แอซิด เวลิกเซล โครงสร้างทรงกลมรวมถึงคุณสมบัติทางสีที่สำคัญของเวลิกเซลยังคงสภาพในฟิล์ม กลไกการเปลี่ยนสีของพอลิไดอะเซทิลีนเวลิกเซลศึกษาโดยการดูดกลืนแสงระบุนการเปลี่ยนแปลงของหมู่ข้างเคียงของพอลิเมอร์สองชนิด ได้แก่ การเปลี่ยนแปลงที่ผันกลับได้ของสายโซ่แอลิฟาติกและการเปลี่ยนแปลงที่ผันกลับไม่ได้ของการสลายพันธะไฮโดรเจน ในการเปลี่ยนแปลงสีโดยอุณหภูมิ กลไกการเปลี่ยนสีเริ่มจากการเปลี่ยนคอนฟอร์เมชันของหมู่ข้างเคียงแบบผันกลับได้ซึ่งทำให้เกิดเวลิกเซลสีม่วงตามด้วยการสลายตัวของพันธะไฮโดรเจน ในการเปลี่ยนแปลงสีตามตัวทำละลายเอทานอลและค่าความเป็นกรด กลไกการเปลี่ยนสีเริ่มจากการรบกวนที่พื้นผิวของเวลิกเซลโดยตรงทำให้พันธะไฮโดรเจนแตกออก เซ็นเซอร์ตรวจจับไอออนของตะกั่วชนิดที่มีความจำเพาะเจาะจงสูงซึ่งพัฒนาขึ้นโดยอาศัยการเพิ่มความว่องไวต่อแรงกระทำที่พื้นผิวของพอลิไดอะเซทิลีนด้วยสารประกอบเอสเทอร์ระหว่าง ไตรเอทิลีนไกลคอลกับ 10,12-เพนตะโคไซด์อายโนอิก แอซิด นอกจากนี้ สีสกรีนที่เปลี่ยนแปลงตามอุณหภูมิยังได้รับการพัฒนาจาก พอลิไดอะเซทิลีนเพื่อใช้เป็นฉลากที่ว่องไวต่ออุณหภูมิ

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Polydiacetylene (PDA) is an interesting class of conjugated polymer having unique chromic properties suitable for many sensing applications. Although extensive research in PDA for sensing applications have been reported, there is still research gaps in understanding of its color transition mechanism and developing it into a convenient to use platform with high sensitivity and selectivity. In this dissertation, polyelectrolyte multilayer (PEM) thin films using either chitosan or poly(ethylenimine) as a polycation and polymerized 10,12-pentacosadiynoic acid vesicles (poly(PCDA)) as a polyanion are successfully prepared. The spherical structures of vesicles, as well as their important chromic properties are retained in the PEM films. Color transition mechanism of poly(PCDA) vesicles probed by electronic absorption spectroscopy indicates two types of sidechain movement: the reversible conformational change of the aliphatic chains and the irreversible hydrogen bond breaking. In the thermochromism, the transition starts with reversible conformational alteration of methylene side chains leading to metastable purple vesicles followed by the hydrogen bonds breaking. In the ethanolochromism and alkalinochromism, the processes are however induced at the vesicle-media interface, directly bringing about the hydrogen bond breaking. The highly selective colorimetric lead ion sensor is developed based on the interaction at the poly(PCDA) vesicle surface using triethylene glycol ester of PCDA (TEGPCDA) as the sensitivity enhancer. Furthermore, thermochromic screen ink is also developed from poly(PCDA) for temperature sensitive labeling.

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## List of Abbreviations and Signs

|                      |                                   |
|----------------------|-----------------------------------|
| Å                    | Angstrom                          |
| AFM                  | Atomic force microscopy           |
| $^{13}\text{C}$ -NMR | Carbon nuclear magnetic resonance |
| cm                   | Centimeter                        |
| $\delta$             | Chemical shift                    |
| %CR                  | % Colorimetric response           |
| $J$                  | Coupling constant                 |
| $^{\circ}\text{C}$   | Degree celsius                    |
| DLS                  | Dynamic light scattering          |
| g                    | Gram                              |
| Hz                   | Hertz                             |
| kcal                 | Kilocalorie                       |
| mL                   | Millilitre                        |
| mmol                 | Millimole                         |
| M                    | Molar                             |
| nm                   | Nanometer                         |
| ppm                  | Part per million                  |
| $\text{cm}^{-1}$     | Per centimetre                    |
| $\text{M}^{-1}$      | Per molar                         |
| $^1\text{H}$ -NMR    | Proton nuclear magnetic resonance |
| TEM                  | Transmission electron microscope  |
| UV/vis               | Ultra violet-visible              |
| $\lambda$            | Wavelength                        |



### List of Numbered Compounds

|                               |                                                         |
|-------------------------------|---------------------------------------------------------|
| <b><math>\alpha</math>-CD</b> | alpha-cyclodextrin                                      |
| <b>AEPCDA</b>                 | aminoethyl-10,12-pentacosadiynamide                     |
| <b>PCDANH<sub>2</sub></b>     | aminoethyl-10,12-pentacosadiynamide                     |
| <b>CHO</b>                    | cholesterol                                             |
| <b>EBPCDA</b>                 | <i>N,N'</i> -ethylene-bis-(10,12-pentacosadiynamide)    |
| <b>MPCDA</b>                  | methyl-10,12-pentacosadiynoate                          |
| <b>PCDA</b>                   | 10,12-pentacosadiynoic acid                             |
| <b>PC</b>                     | phosphatidylcholine                                     |
| <b>PAH</b>                    | poly(allylamine hydrochloride)                          |
| <b>PDA</b>                    | polydiacetylene                                         |
| <b>PEM</b>                    | polyelectrolyte multilayer                              |
| <b>PEI</b>                    | poly(ethylenimine)                                      |
| <b>Poly(PCDA)</b>             | poly(10,12-pentacosadiynoic acid)                       |
| <b>Poly(TCDA)</b>             | poly(10,12-tricosadiynoic acid)                         |
| <b>PCDA-mBza</b>              | 10,12-pentacosadiynamide of <i>m</i> -aminobenzoic acid |
| <b>PSS</b>                    | poly(styrene sulfonate)                                 |
| <b>PVA</b>                    | poly(vinyl alcohol )                                    |
| <b>PVC</b>                    | poly(vinyl chloride)                                    |
| <b>SLO</b>                    | steptolysin                                             |
| <b>TEGPCDA</b>                | triethylene glycol ester of-10,12-pentacosadiynoic acid |