Journal of Industrial and Engineering Chemistry 23 (2015) 279–284

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Sensitivity limitation of the sensor fabricated with polydiacetylene

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ARTICLE INFO

Article history:
Received 25 July 2014
Accepted 31 August 2014
Available online 6 September 2014

Keywords:
Polydiacetylene
Vesicle
Sensor
Sulfonate
Amine

ABSTRACT

In order to estimate the sensitivity limitation of the polydiacetylene (PDA) sensor system, the response of the PDA system to several sulfonate salts and amines were examined. The PDA systems were fabricated with *N*-(2-aminoethyl)pentacosa-10,12-diynamide (AEPCDA) and 10,12-pentacosadiynoic acid (PCDA). The functional group at the end of the PDA system is crucial to sensing the substrate because this functional group interacts with the substrate. The sensitivity limitation toward the molecular weight and the concentration of the substrate is also revealed. The pK_a of the amines is less crucial to the sensing than the molecular weight of the substrate.

Introduction

Polydiacetylenes (PDA) have been widely investigated as smart sensing materials because of their unique optical properties [1–3]. PDA sensor systems can be easily fabricated by forming the vesicle system from the sonication of the amphiphilic compound containing diacetylene moiety and following the photopolymerization. In this photopolymerization the initiator is not necessary and UV irradiation is enough to initiate the polymerization. The aligned monomeric diacetylene lipids undergo a photopolymerization process by UV irradiation via a 1,4-polymerization mechanism to form π-conjugated polymer chains that give the material a colored appearance. PDA exhibits a distinctive chromatic transition upon stimulation by temperature increase, mechanical stress, or chemical materials. Sensing technologies based on colorimetric response are very attractive because they can be noted by the naked eye and hence do not require expensive devices or equipment. Various sensing systems for special chemical materials, such as mercury(II) [4], melamine [5], warfare gas [6], toxin [7], nucleic acid [8], adulterated gasoline [9], potassium [10], and antibiotics [11] were developed by researchers using the properties of PDAs.

Until now the reported sensing mechanism for the PDA vesicle system is that the polymerized compound is dislocated after applying the stimulation, and therefore the length of the conjugated unsaturated bond in the PDA system is decreased. This result shows the color change from blue to red. Even though many research results were reported, the sensitivity limitation of the PDA sensor is not still defined clearly. In this study, in order to estimate the sensitivity limitation of the PDA sensor precisely, the sensing experiments for the several PDA systems were conducted using diverse sulfonate salts and various amine compounds as the substrates.

Experimental

Materials and instruments

10,12-pentacosadiynoic acid (PCDA), *N*-hydroxysuccinimide, *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide, ethylenediamine, sodium *p*-toluenesulfonate (SPTS), sodium antheaquinone-2-sulfonate (SAQS), sodium dodecylbenzenesulfonate (SDBS), butylamine, hexylamine, dibutylamine, and octylamine were purchased from Sigma-Aldrich. Nuclear magnetic resonance spectroscopy (NMR) was performed using a DPX 300 (Bruker), and infrared spectroscopy (IR) was performed using a FT-IR 680 (Jasco International). Cole-Parmer 4710 250 W sonicator was used for sonication to form the vesicle suspension.

Synthesis of N-*(2-aminoethyl)pentacosa-10,12-diynamide (AEPCDA)*

AEPCDA was synthesized using PCDA as a starting material by already reported methods [12–14].

NMR data: 0.89 (t, 3*H*), 1.29 (s, 26*H*), 1.45–1.53 (m, 6*H*), 2.14 (t, 2*H*), 2.24 (t, 4*H*), 2.82 (m, 2*H*), 3.35 (m, 2*H*), 4.49 (s, 2*H*), 6.43 (s, 1*H*).

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http://dx.doi.org/10.1016/j.jiec.2014.08.029
1226-086X/

The formation of the vesicle solution

The PDA vesicles were prepared as follows. The monomeric compound (AEPCDA and PCDA) was dissolved in chloroform and then filtered, using a 0.50 μm filter, to remove residual polymers. The filtered solution was slowly dried at 50 °C under vacuum to form a film at the bottom of the flask. After all of the chloroform was evaporated, some deionized water was added into the flask to provide 1.0 mM concentration of the solution. And then the sample was sonicated at 90 °C for 20 min to disperse the monomeric compound into aqueous medium, and then the vesicle solution was formed finally. The vesicle solution was allowed to cool to room temperature and then kept at 4 °C overnight in the refrigerator. In order to polymerize the vesicle, the vesicle was illuminated by UV light (254 nm) for 15 s (AEPCDA) and 40 s (PCDA).

The detecting of the substrates by PDA vesicle systems

The color transition was examined using the formed vesicle system, and the sulfonate salts and amines were used as substrates. The solutions of the substrates were added to the vesicle solutions. The final concentrations of the sulfonates and amines were adjusted within the range from 10 μM to 500 μM. The color changes were recorded using photographs and were also recorded using the UV spectrometer.

Result and discussion

The formation of the PDA vesicle systems

PCDA and AEPCDA were used as the diacetylene compounds and three kinds of sulfonate salts and four kinds of amines were used as the substrate for detecting. The chemical structures of all of these compounds are shown in Fig. 1.

In Fig. 1, SPTS is the sulfonate which has one benzene ring, SAQS is the sulfonate which gets the size with the three benzene rings attached consecutively, and SDBS is the sulfonate which has one benzene ring and long carbon chain containing 12 carbons. The amines used in this study have 4 to 8 carbons.

The vesicle systems were fabricated by sonication using PCDA and AEPCDA, respectively. And the photopolymerization was conducted by UV illumination. During the polymerization the color of the solution changed from colorless to blue.

The detecting of the sulfonates

PCDA has a carboxylic acid functional group at the end of the compound. After the formation of the PDA system using PCDA, the carboxylic acid functional groups cover the all surface of the vesicle system. First after the PDA system was fabricated using PCDA, the detecting experiments were conducted using the sulfonates as the substrates. The results are shown in Fig. 2.

In Fig. 2, these vesicle systems did not show any color change for all of the sulfonates used in this study. There are no interaction between the PCDA-based PDA system and the sulfonate used in this study.

As a next experiment, AEPCDA was used as an amphiphilic compound to form the vesicle system. AEPCDA has an amine functional group at the end of the compound. After the PDA system was fabricated using AEPCDA, the detecting experiments were conducted using sulfonates as the substrates. The results are shown in Fig. 3.

Unlike the PCDA-based PDA system, AEPCDA-based PDA system showed color change for some of the sulfonates. In Fig. 3, SPTS did not show any color change at 10 μM and also did not show any

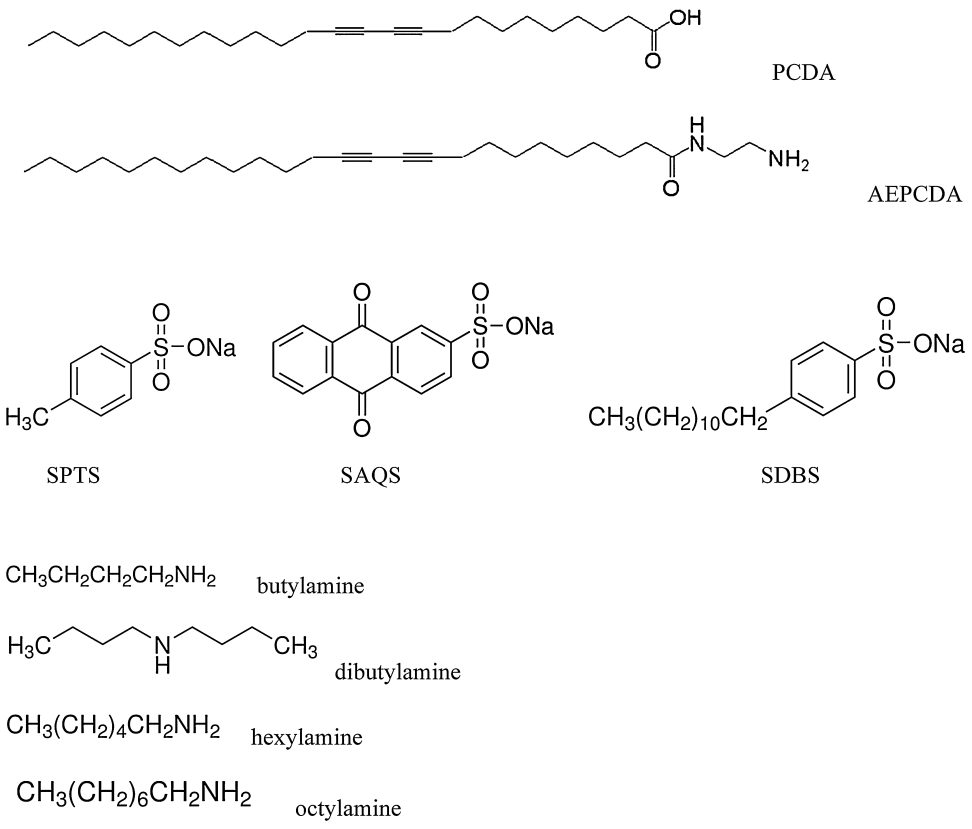

Fig. 1. The chemical structures of diacetylene compounds and sulfonates used in this study.