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Colorimetric sensing of various organic acids by using polydiacetylene/zinc oxide nanocomposites: Effects of polydiacetylene and acid structures

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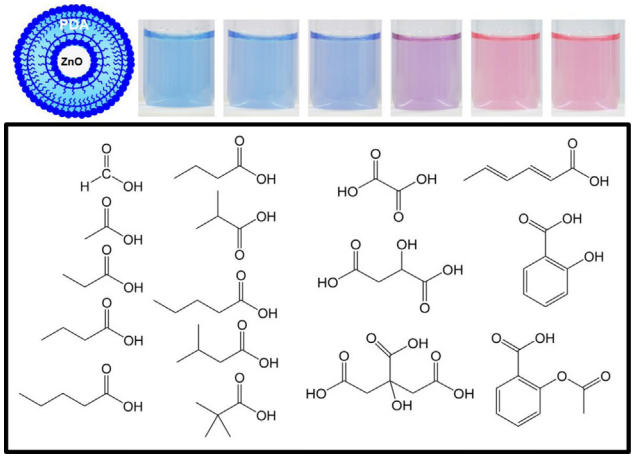
HIGHLIGHTS

- Polydiacetylene(PDA)/ZnO nanocomposites exhibit color-transition upon exposure to various organic acids.
- The color-transition behaviors depend on the side chain length of PDAs and acid structure.
- Increasing chain length of the acids promotes the color-transition.
- Number of carboxylic group and methyl branch in the acids strongly affects the color-transition behaviors.
- These nanocomposites can be utilized for detecting organic acids commonly used in industries.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we utilize the polydiacetylene(PDA)/zinc oxide(ZnO) nanocomposites as colorimetric sensors of various organic acids. Series of organic acids with systematic variation of molecular structure and dissociation constant (K_a) are investigated. The PDA/ZnO nanocomposites are prepared by using three types of monomer with different alkyl chain length, 5,7-hexadecadiynoic acid, 10,12-tricosadiynoic acid and 10,12-pentacosadiynoic acid. Our results show that all PDA/ZnO nanocomposites exhibit color transition upon the addition of organic acids with concentration ranging from 0.01 to 100 mM. By varying PDA structures, detection of each acid at desired concentrations can be controlled. The color transition of the nanocomposites depends significantly on the dissociation ability and structure of acids. For linear alkanoic acids, PDA/ZnO nanocomposites exhibit higher sensitivity to the acids with higher K_a value. When the K_a values are comparable, the architecture of organic acids becomes a dominant factor. Acids with longer chain length induce the color transition of PDA/ZnO nanocomposites at lower concentration. However, acids with branch structure cause an opposite result. The amount of carboxylic group in acids

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also plays an important role on the color-transition behaviors. The colorimetric response of PDA/ZnO nanocomposites upon exposure to common organic acids used in industries including sorbic acid, oxalic acid, malic acid, citric acid, salicylic acid and acetylsalicylic acid are also investigated.

1. Introduction

Organic acids are generally used in food, drug and cosmetic industries. For example, lactic acid, citric acid, acetic acid and tartaric acid have been described as strong antimicrobial agents against psychrophilic and mesophilic microorganisms in fresh-cut fruits and vegetables [1]. Butyric acid esters have been extensively used as flavor additives to increase fruit-like fragrance in food [2]. Propionic acid has been used as a preservative and also an ingredient in animal feeds, plastics, herbicides, pharmaceuticals and perfumes [3]. Sorbic acid is a common preservative in a great varieties of food such as non-alcoholic drinks, grape juice, dried fruits and vegetables [4]. It has been known that the excessive use of these additives could lead to adverse effects such as metabolic acidosis, convulsions and hyperpnoea in humans. Therefore, an effective method for detection of organic acids is extremely important in the food industries. The general methods reported so far have been based on gas chromatography [4–7] and high performance liquid chromatography [8–10] techniques. Although these methods can provide high resolution result, they generally require multistep procedures that are complicate and time-consuming.

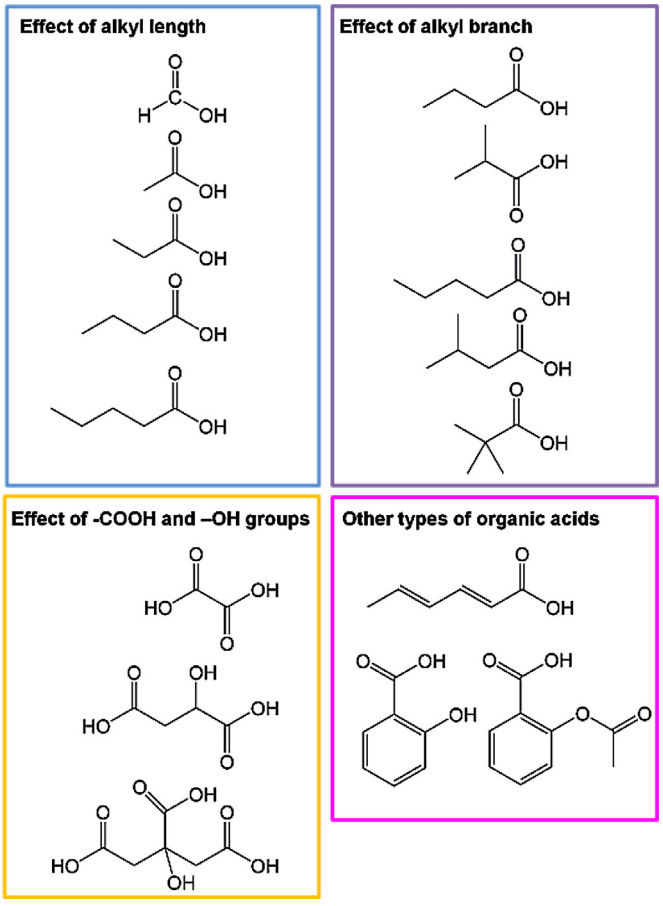

Fig. 1. Chemical structure of organic acids used in this study.

The development of sensing materials based on colorimetric response is rather attractive for the food industries. This is mainly due to the simplicity of their utilization. The change of color upon exposing to stimuli can be easily observed by naked eyes or detected by simple devices. Polydiacetylene (PDA) is a class of conjugated polymer that is very promising to utilize as colorimetric sensors [11–19]. It has been observed that the PDAs exhibit color transition when subjected to solvents [20–25], chemicals [26–29], heat [16,17,21,30–38], ions [39–44] and pH [21,45–51]. In general, the commercially available PDAs with carboxylic head groups exhibit color transition in basic condition [21,47]. The decrease of pH does not cause any color transition but instead induces agglomeration. Structural modification of PDAs is an effective method for improving the colorimetric response to acids [45,46,49,50]. Seo and Kim fabricate PDA assemblies from a series of *N*-(*n*-aminoalkyl)-10,12-pentacosadiynamide [50]. In this system, the presence of amino head groups causes these PDAs to change their color upon the addition of alkanoic acids. Although the structural modification of PDAs is a very effective method for controlling their color-transition behaviors, it normally requires complicate synthetic route, expensive chemicals and a time consuming purification process. These become major problems in mass production for the industrial scale utilization.

Recently, our group has shown that the incorporation of zinc oxide (ZnO) nanoparticles into PDA assemblies results in drastic change of their color-transition behaviors [30–33,51]. The PDA/ZnO nanocomposites exhibit color transition at higher temperature compared to their pure PDA counterparts and also show thermochromic reversibility. In addition, the PDA/ZnO nanocomposites change color upon addition of hydrochloric acid (HCl) while the pure PDA vesicles remain unchanged [51]. In this continuation study, we take a step forward to demonstrate the utilization of PDA/ZnO nanocomposites as colorimetric sensors for organic acids commonly used in industries. Various types of organic acid are used in order to investigate the effects of structure and dissociation ability on the color transition of PDA/ZnO nanocomposites. The length of linear alkanoic acids is varied from 1 to 5 carbon atoms. The effects of methyl branch and —COOH group in the organic acids are also investigated. Our results demonstrate that the color transition of PDA/ZnO nanocomposites occurs at different pH and acid concentration compared to the use of HCl acid in the previous study [51]. The PDA/ZnO nanocomposites are prepared from three monomers, 10,12-pentacosadiynoic acid (PCDA), 10,12-tricosadiynoic acid (TCDA) and 5,7-hexadecadiynoic acid (HDDA) to investigate the effects of alkyl side chain length on the color-transition behaviors. Our study provides fundamental knowledge about the structural–property relationship between organic acids and the color transition of PDA/ZnO nanocomposites.

2. Experimental

The DA monomers used in this study, 5,7-hexadecadiynoic acid (HDDA), 10,12-tricosadiynoic acid (TCDA) and 10,12-pentacosadiynoic acid (PCDA), were commercially available at Fluka. The ZnO nanoparticles with average diameter of 65 ± 27 nm were purchased from Nano Materials Technology (Thailand) [30] (See supporting information for particle size distribution of ZnO).