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Utilization of polydiacetylene/zinc oxide nanocomposites to detect and differentiate organic bases in various media

Amornsak Chanakul^a, Rakchart Traiphol^{b,c,d}, Nisanart Traiphol^{a,*}

^a Laboratory of Advanced Chromic Materials, Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

^b Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand

^c Laboratory of Advanced Polymers and Nanomaterials, School of Materials Science and Engineering and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University at Salaya, Phuttamonthon 4 Road, Salaya, Nakhon Pathom 73170, Thailand

^d NANOTEC-MU Excellence Center on Intelligent Materials and Systems, Faculty of Science, Mahidol University, Rama 6 Road, Ratchathewi, Bangkok 10400, Thailand

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ABSTRACT

Polydiacetylene/zinc oxide (PDA/ZnO) nanocomposites are demonstrated as colorimetric sensors for organic bases. Influence of stimuli structure on the color-transition behaviors is investigated. Addition of methylamine, ethylamine, butylamine and pentylamine into pure PDAs with different alkyl chain length induces blue-to-red transition at the same concentration. Interestingly, for PDA/ZnO, it shows an ability to differentiate these alkylamines. The detecting concentration and the ability to differentiate the alkylamines can be controlled by adjusting the alkyl chain length of PDA/ZnO. Moreover, PDA/ZnO-embedded paper is successfully fabricated and used to detect alkylamines in different media. Results extend the utilization of PDA-based materials in sensing technologies.

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Introduction

Aliphatic amines are widely used in many chemical industries such as fertilizer, herbicides, pesticides, pharmaceuticals, surfactants, rubber latex and colorants [1–3]. It is known that these organic compounds exhibit rather high toxicity. They can readily access the brain and spinal tissues and interfere with neurological function [4]. Pyridine is released into environments via different pathways such as coal gasification, pesticide use and manufacture of dyes [5,6]. The pyridine can cause severe health hazards such as an increase in heart rate, heart disease and stroke [5]. Many methods have been utilized for detecting these organic bases, including electrochemical [7,8], quartz crystal microbalance [9], enzymatic [10], optical spectrophotometry [11], polymer-based sensing techniques [12], liquid chromatography–mass spectrometry [13] and gas chromatography–mass spectrometry [14]. Although these methods can provide highly effective results, they require complicated instrumentation. Due to its simplicity, sensing material based on colorimetric response is rather attractive for this application.

Polydiacetylenes (PDA) have been known for their utilization as colorimetric sensors [15–23]. PDAs can change color upon exposure to solvents [24–29], surfactants [30–33], heat [20,25,34–42], ions [43–48] and acids and bases [25,49–56]. In general, the color transition of PDAs with carboxylic head groups occurs in a basic condition [25,51]. This is mainly due to the reaction between OH[−] ions and the carboxylic head groups, inducing the rearrangement of PDA segments. Our recent studies have shown that the color-transition behaviors of PDAs can be systematically controlled by incorporating zinc oxide (ZnO) nanoparticles into the systems [34–37,55]. Although the original PDAs do not change color in acidic condition, the PDA/ZnO nanocomposites exhibit a clear color transition upon addition of various acids [55,57]. In basic condition, color transition of the nanocomposites takes place at much higher pH compared to those of their pure constituent PDAs. The presence of strong interfacial interactions within PDA/ZnO nanocomposites also results in drastic increase of their color stability. When the nanocomposites are dispersed in various organic media or polymer matrices, their original blue color as well as reversible thermochromic property are hardly affected [37]. Our results can extend their utilization in different areas of sensing technology.

In this continuation effort to develop this class of materials, we demonstrate that the PDA/ZnO nanocomposites can be used to

* Corresponding author. Fax: +66 2 2185561.

E-mail addresses: Nisanart.T@chula.ac.th, nannisanart@yahoo.com (N. Traiphol)

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detect and differentiate organic bases in various media including water, milk and toluene. A series of aliphatic amines and pyridine are used for investigating the effects of molecular size on the color-transition behaviors. Pure PDAs and PDA/ZnO nanocomposites are prepared from three types of monomers, 10,12-pentacosadiynoic acid (PCDA), 10,12-tricosadiynoic acid (TCDA) and 5,7-hexadecadiynoic acid (HDDA). Their chemical structures are illustrated in Supporting information. The color-transition behaviors of these materials are investigated in suspension and paper-embedded forms. Our results show that the PDA/ZnO nanocomposites can be used to detect various organic bases at relatively wide concentration range. They can also differentiate the organic bases, depending on their individual molecular architecture. The mechanism involving the color-transition behaviors of these systems is investigated by utilizing different techniques. Our results in this study provide fundamental understanding, which is important to further expand the utilization of PDA-based materials in base-sensing applications.

Experimental

The DA monomers and ZnO nanoparticles used in this study were commercially available [34,35]. The physical properties of aliphatic amines and pyridine (AR grade, Aldrich) are listed in Table 1. The pure PDAs and PDA/ZnO nanocomposites were prepared and characterized as described in our previous reports [34–37,55]. The pure PDAs and PDA/ZnO nanocomposites were fabricated into thin films by soaking small pieces of filter papers (Whatman No. 4) in their aqueous suspensions for 30 s followed by air-drying. The process was repeated 10 times for pure PDAs and 5 times for the nanocomposites.

The color-transition behaviors of pure PDAs and the nanocomposites are followed by using UV/vis absorption spectrometer (Analytik Jena Specord S100). Concentration of the PDA and the nanocomposite suspensions in all experiments is controlled to be the same. The addition of organic bases into pure PDA and nanocomposite suspensions was carried out by using micropipette. Prior to each measurement, the suspensions were stirred and incubated for about 5 min.

Results and discussions

Color-transition behaviors of pure PDAs

It is known that the PDAs with carboxylic head groups exhibit color transition upon exposure to various bases [51,55,56,59]. In this first section, the colorimetric response of poly(TCDA) vesicles to NaOH and organic bases is investigated for comparison purpose. The addition of NaOH induces complete color transition to red phase at ~ 1.15 mM (see Supporting information). When the alkylamines are used, the colorimetric response takes place at a lower concentration region. Fig. 1a shows absorption spectra of poly(TCDA) measured upon increasing the concentration of methylamine. A small peak at 540 nm is detected at ~ 0.08 mM of methylamine and continuously grows upon further increasing the concentration. A complete change to red color is observed at the concentration of ~ 0.77 mM. The plots of CR values as a function

of base concentration are illustrated in Fig. 1c. Since methylamine and NaOH have different dissociation constants (pK_b), the colorimetric response of poly(TCDA) may varies with the OH^- concentration in the suspension. We detect the color transition at different pH values as shown in Fig. 1d. The color transition of methylamine and NaOH systems occurs at pH about 8.5 and 9.5, respectively. It requires much lesser OH^- concentration in the system of methylamine to induce the color transition. This result indicates the important role of the stimuli structure on color-transition behaviors of poly(TCDA) vesicles. We have observed that the increase of hydrophobic tail accelerates the color-transition process of PDA assemblies in aqueous suspension [24,57].

The addition of other aliphatic amines with longer alkyl length including ethylamine, butylamine and pentylamine also causes the blue-to-red color transition. However, the colorimetric response of poly(TCDA) vesicles is similar to that of the methylamine system. The color transition of these systems occurs at similar concentration and pH values as shown in Fig. 1c and d. Our observation suggests that the increase of alkyl chain length of these organic bases has a negligible effect on the color-transition behaviors of pure poly(TCDA) vesicles. In other words, the pure poly(TCDA) cannot differentiate this series of linear alkylamine. A similar result is also observed in the system of pure poly(PCDA) (see Supporting information). It is important to note that the effect of alkylamine structure on the sensitivity of pure poly(PCDA) vesicles has been previously investigated by different research groups [56,59]. They have demonstrated that the linear alkylamine with longer hydrophobic tail induces the color transition at lower concentration. The longer alkylamine can penetrate into the deeper hydrophobic region of poly(PCDA) layer, causing larger perturbation to the system. However, the length of alkylamines used in the previous studies are much longer compared to our system.

When pyridine is used as a stimulus, the color transition occurs at much higher concentration compared to the systems of linear alkylamines. The absorption spectra measured upon the addition of pyridine exhibit a small peak at 540 nm when the concentration reaches 39.6 mM (see Fig. 1b). A complete blue-to-red color transition occurs at 210 mM. However, pyridine is a very weak alkaline with much lower dissociation ability compared to those of the alkylamines (see Table 1). When the CR values are plotted as a function of pH, the color-transition region is detected at about 7.8, which is lower than the systems of linear alkylamines (see Fig. 1d). This result further illustrates the important role of stimuli architecture on the color transition behaviors of PDAs assemblies.

Color-transition behaviors of PDA/ZnO nanocomposites

Our previous study has shown that the color transition of PDA/ZnO nanocomposites upon addition of NaOH occurs at much higher pH compared to their pure constituent PDAs [55]. We observe similar behavior when the linear alkylamines are used as stimuli. Fig. 2 shows the variation of absorption spectra of the nanocomposites upon addition of butylamine. For the poly(TCDA)/ZnO nanocomposite, a complete blue-to-red color transition is observed at ~ 210 mM while it requires ~ 0.77 mM in the system of pure poly(TCDA) vesicles. The comparison of pure poly(PCDA) vesicles and poly(PCDA)/ZnO nanocomposite shows similar trend. However, with slightly longer alkyl chain length, the color transition of poly(PCDA)/ZnO nanocomposite occurs at higher concentration of butylamine compared to that of the poly(TCDA)/ZnO nanocomposite. A complete red phase of poly(PCDA)/ZnO nanocomposite is obtained when the butylamine concentration reaches ~ 980 mM. In the system of poly(HDDA)/ZnO nanocomposite, which constitutes the shortest alkyl side chain, the complete color transition occurs at much lower butylamine concentration, ~ 18.6 mM.

Table 1
Physical properties of organic bases used in this study [58].

| Organic bases | pK_b | Solubility |
|---------------|--------|------------|
| Methylamine | 3.34 | Miscible |
| Ethylamine | 3.35 | Miscible |
| Butylamine | 3.40 | Miscible |
| Pentylamine | 3.37 | Miscible |
| Pyridine | 8.77 | Miscible |

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