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Formation of Polydiacetylene/Silica Nanocomposite as a Colorimetric Indicator: Effect of Time and Temperature

A. NOPWINYUWONG

Department of Packaging and Materials Technology, Faculty Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

W. BOONSUPTHIP

Department of Food Science and Technology, Faculty Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

Center for Advanced Studies in Agriculture and Food, KU Institute for Advanced Studies, Kasetsart University, Bangkok 10900, Thailand

C. PECHYEN, P. SUPPAKUL

Department of Packaging and Materials Technology, Faculty Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

Center for Advanced Studies in Agriculture and Food, KU Institute for Advanced Studies, Kasetsart University, Bangkok 10900, Thailand

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Correspondence to: C. Pechyen; e-mail: chiravoot.p@ku.ac.th.

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ABSTRACT: This work presents a method to prepare a new class of polydiacetylene (PDA)/SiO_2 nanocomposites for colorimetric indicator applications. The silica concentration is 5 wt% of the diacetylene monomer, 10,12-pentacosadiynoic acid (PCDA). Under ultraviolet light irradiation, PCDA vesicle/silica nanocomposites were formed and an intense blue solution was obtained. The silica nanoparticles can improve chromic properties of molecules. The color transition of PDA/silica nanocomposites can change from blue ($\lambda_{max} \sim 640$ nm) to red ($\lambda_{max} \sim 540$ nm), which is irreversible when stored at different temperatures and time. This study investigated characterization of the aqueous suspension compared with pure PDA vesicles in the absorption spectra. Moreover, the color response was calculated. This is an efficient method for preparation of the colorimetric sensor of nanocomposite materials after UV irradiation. The PDA/5 wt% silica nanocomposites aqueous matrix would potentially be developed as a new colorimetric polymeric indicator to study the effect of temperature and time. © 2012 Wiley Periodicals, Inc. Adv Polym Techn 32: E724–E731, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21315

KEY WORDS: Indicator, Polydiacetylene, Silica nanoparticle, Thermochromism, UV–vis spectroscopy

Introduction

Various detection methods have attracted attention to develop the diagnostic tools that can rapidly screen the specific target factors in pharmaceutical and drug analyses, food industries, and the environment.[1,2] Various detection methods can be colorimetric, fluorescent, and electrochemical methods.[3] Particularly, the colorimetric detection method does not require expensive equipment and it is easily observed with the naked eye, so this detection method is the most convenient method.[4] Polydiacetylene (PDA) is widely known as a colorimetric polymeric material because it can be used as an excellent color-changing indicator for temperature, chemicals, and biological agents. PDAs are an interesting class of conjugated polymers that can be prepared from vesicles of 10,12-pentacosadiynoic acid (PCDA). PCDA monomers not only consist of the hydrophilic carboxylic group that generally binds with water but also contain hydrophobic groups that have a long hydrocarbon chain.[5] PDAs are prepared by using photopolymerization of self-assembled PCDA monomers in the form of lipid bilayer vesicles. Under UV irradiation, they are formed by the addition of the PCDA monomers and then have alternating double- and triple-bond groups in the main polymer chain (Fig. 1a).[6–8] Delocalized enyne backbones of molecularly ordered PDA side chains induce a blue-to-red color change.[9] Before polymerization, PDA cannot show absorption in the visible region. After that, the PDA appears blue, with a maximum absorption at about 640 nm. The color transitions can be significantly shifted during absorption from low- to high-energy bands of the visible spectrum, where the PDA transforms from blue to red, with a maximum absorption at about 540 nm.[10–12] The color transitions of PDAs can result from rotation of the C—C bond of the polymer backbone, which occurs via a linear π-orbital conjugated backbone in its planarity. When the rotation changes few degrees of the π-orbital overlap, it results in a significant blueshift of the absorption spectrum.[7,12–16] Finally, PDAs appear purple and red to the naked eyes.

The forms of PDAs can be structured in liposomes,[17] vesicles,[18] monolayer films such as Langmuir–Blodgett films,[12,19] multilayer films,[20] and nanocomposites integrated into inorganic polymers.[21] Based on the knowledge of the PDA's structure, it can be prepared in a vesicle form that is homogeneously dispersed in water. The high polar carboxylic head groups can interact with hydroxyl groups of water that surrounds the groups. On the other hand, the nonpolar hydrocarbon chain of both PDCA molecules will arrange near each other and produce ordered bilayer vesicle forms.[17,18,21] Upon various external stimuli, the PDAs' molecules exhibit strong optical absorption

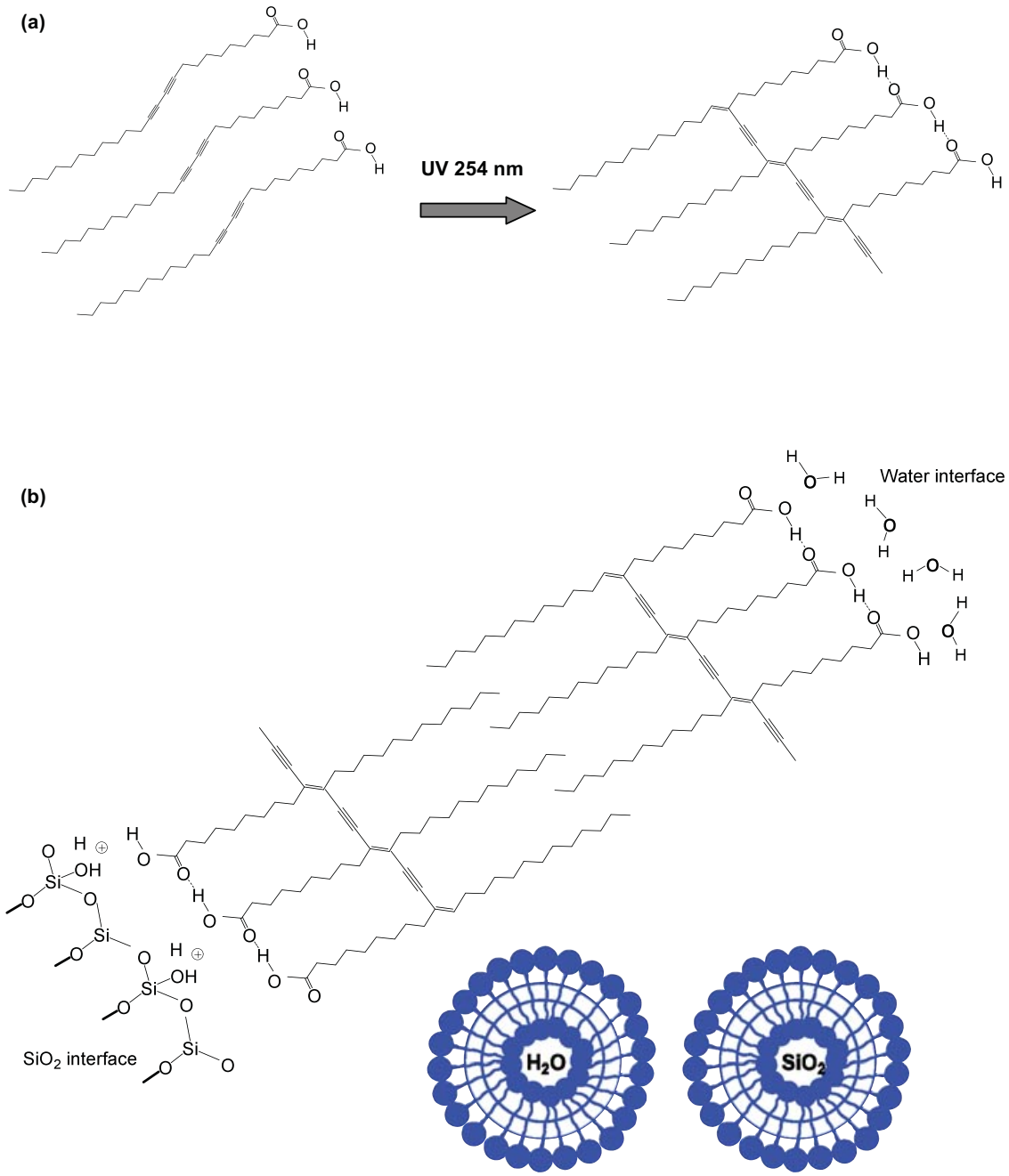

FIGURE 1. Polymerization of PCDA monomers after UV light irradiation (a) and the PDA/SiO_2 nanocomposites dispersed in water in which silica nanoparticles move into the core of PDA vesicles (b).

and generate a blue-to-red transition mechanism, namely photochromism (light),[11] thermochromism (heat),[22–25] mechanochromism (mechanical stress),[26] solvatochromism (organic solvents),[25,27] and affinochromism/biochromism (binding of specific chemical or biological targets).[28,29] Recently, these mechanisms of PDA molecules were developed for nanocomposite application by adjustable chromatic properties. Su[30] reported that the silica nanoparticles could prevent aggregation and improve an ordered arrangement of PCDA molecules. At 640 nm, the absorbance intensity of the PCDA/silica nanocomposites in aqueous solution increased compared with pure PCDA molecules after UV irradiation. Traiphol et al.[31] investigated the addition of ZnO nanoparticle as

a nanosubstrate for self-assembly, which could manipulate color transition of PDA vesicles. The PDA/ZnO nanocomposites exhibited a two-step color transition with increasing temperature.

In this work, the irreversible thermochromism of PDA vesicles and the addition of silica nanoparticles into PDA vesicles are investigated. Moreover, the effects of concentration of amphiphilic polymer, temperature, and time on the color transition of PDA/silica nanocomposites were studied using the UV–vis spectroscopy technique. The color response (CR) evaluated the relative color changes from the initial percentage of blue to the final percentage of blue after preparation of the PDA/silica nanocomposites.

Experimental

MATERIALS

PCDA was purchased from Fluka (St. Louis, MO) and purified by dissolving it in chloroform. Chloroform ($CHCl_3$) and Pluronic F127 were purchased from Lab-Scan (Gliwice, Poland) and Sigma (St. Louis, MO), respectively. Poly(ethylene glycol) (PEG400, molecular weight = 400) was provided by Siam Chemical Industry (Bangkok, Thailand). In addition, untreated silica nanopowder (Aerosil® 200), which have a particle size in the range of 12–40 nm, is commercially available from National Metal and Materials Technology Center (Bangkok, Thailand).

PREPARATION OF PDA/SILICA NANOCOMPOSITES

The PCDA monomer was dissolved in chloroform in a round-bottomed flask. The chloroform solution was removed by using a rotating evaporator until a lipid layer was formed. The silica nanocomposites/PCDA were prepared at 5 wt%. Silica nanoparticles were dispersed in deionized water by a sonicator bath for 5 min. The suspension of silica nanoparticles in water was added into the purified PCDA monomer. The concentration of PCDA monomer was adjusted to be about 1 mM. The lipid suspension was ultrasonicated by a sonicator bath at 70°C for 15 min. After that, the solution was cooled and then stored overnight at 4°C to induce crystallization of the lipid membrane. The solution was brought to room temperature and then was irradiated by UV light at 254 nm for 5 min to yield a blue solution of PDA vesicle. Finally, it was stored at 4°C or in a refrigerator until use. The pure PDA vesicles were prepared by the same method without silica nanoparticles.

PREPARATION OF PDA/SILICA NANOCOMPOSITES IN AMPHIPHILIC POLYMER AQUEOUS SOLUTION

0.1 mL of PDA/silica nanocomposites solution was mixed with 0.9 mL of the mixture of Pluronic F127 and PEG400 as an amphiphilic polymer aqueous solution. The various concentrations of F127 were 0, 5, 7.5, 10, and 15% w/v. Then, the mixed solution was placed in a water bath at different temperatures (30–50°C). The color of PDA/silica nanocomposites aqueous solution was observed by comparing it with the pure PDA vesicles/amphiphilic polymer aqueous solution.

SPECTRAL ANALYSIS AND MEASUREMENT OF THE COLOR RESPONSE

The aqueous suspension was taken in a quartz cuvette. The absorption spectra were measured by using a UV–vis spectrophotometer (UV-2450, Shimadzu, Tokyo, Japan). After that the absorbance at 640 and 540 nm was observed at room temperature and the color response (%CR) was calculated by using the following equation:

$$\mathrm{CR}(\%) = \left(\frac{\mathrm{PB}_0 - \mathrm{PB}_1}{\mathrm{PB}_0}\right) \times 100 \qquad (1)$$

PB was calculated from $A_{\mathrm{blue}}/(A_{\mathrm{blue}} + A_{\mathrm{red}})$, where A is the absorbance at either the blue component (640 nm) or the red component (550 nm) of the spectrum, PB_0 is the control, a blue ratio of pure PDA solution at the initial temperature, and PB_1 is the value of sample exposed to different temperatures for different times.

Results and Discussion

It is well known that PDA vesicles can be prepared from self-assembled PCDA monomers, which were produced by UV irradiation without chemical initiators or catalysts, and its structure is prepared in aqueous solution in the form of vesicles or

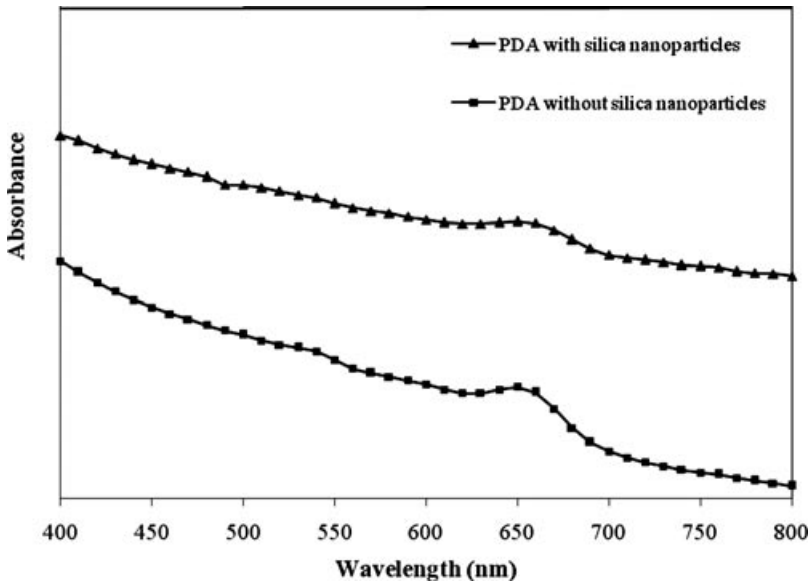

FIGURE 2. Absorption spectra of PDA/silica nanocomposites and pure PDA vesicles at 400–800 nm.

liposomes. It results in a weak interaction between a nonpolar hydrocarbon tail of both monomers and a strong interaction between carboxylic head groups and hydroxyl groups of water, so it can exhibit bilayer vesicle forms. For the incorporation of silica nanoparticles, a functional group of silica nanoparticles strongly interact with PDA vesicles that results due to the interaction between carboxylic head groups and active groups at the silica surface as shown in Fig. 1b. The surface of silica nanoparticles in aqueous solution consists of Si—OH, Si—OH_2^+, and Si—O^- groups that can be driven by an ionic interaction and/or hydrogen bonding.[21,30] In this work, the silica concentration is at 5 wt% of the diacetylene monomer PCDA. The PDA vesicles provided the silica nanoparticles with adjustable thermochromatic properties under UV light at a maximum wavelength of 254 nm. The color of PDA/silica nanocomposites changed from colorless to blue. With the addition of amphiphilic polymers, its hydrophobic segments can be gradually inserted into the lipid monolayer of the PDA vesicles, in which Pluronic polymers as amphiphilic polymers were mixed with the Pluronic F127 and PEG400 to form a poly(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol) copolymer. The Pluronic F127 amphiphilic polymer as a plasticizer can reduce the temperature below 60°C for the color transition of PDA vesicles from blue to red. The color transition of PDA/silica nanocomposites was irreversible and can be observed with the naked eye.

Figure 2 shows the absorption spectra of PDA/silica nanocomposites and pure PDA vesicles in the range of 400–800 nm. The absorbance of PDA/silica nanocomposites was higher than pure PDA vesicles; in particular, the appearance of the blue color in the PDA/silica nanocomposites can exhibit increasing intensity at 630–670 nm. Varying the concentration of Pluronic F127 from 0 to 15% w/v and storing at 30–50°C for 2 days (48 h), gradually decreased the absorption spectra of the blue form ($\lambda_{max} \sim 640$ nm) while the absorption spectra of the red form ($\lambda_{max} = \sim 540$ nm) gradually increased during the storage time. The thermochromic transition showed a hypsochromic shift of λ_{max} (Fig. 3). For example, at 50°C, the PDA/silica nanocomposites gradually produced blue color with the maximum absorption at about 640 nm and its color completely changed to red with the maximum absorption at about 540 nm when the concentration of Pluronic F127 was 15% w/v at different storage time. However, the absorption spectra at 640 nm did not decrease but the absorption spectra at 540 nm gradually increased; thus, the CR, which was calculated following Eq. (1), gradually increased. The CR of the PDA/silica nanocomposites increased early and then became constant after 8 h (or 480 min) when the concentration of Pluronic F127 was constant as compared with pure PDA vesicles as shown in Fig. 4. The higher concentration of Pluronic F127 was observed with higher CR. For example, at 30°C, the CR at 0 and 15% w/v Pluronic F127 and silica nanoparticles was

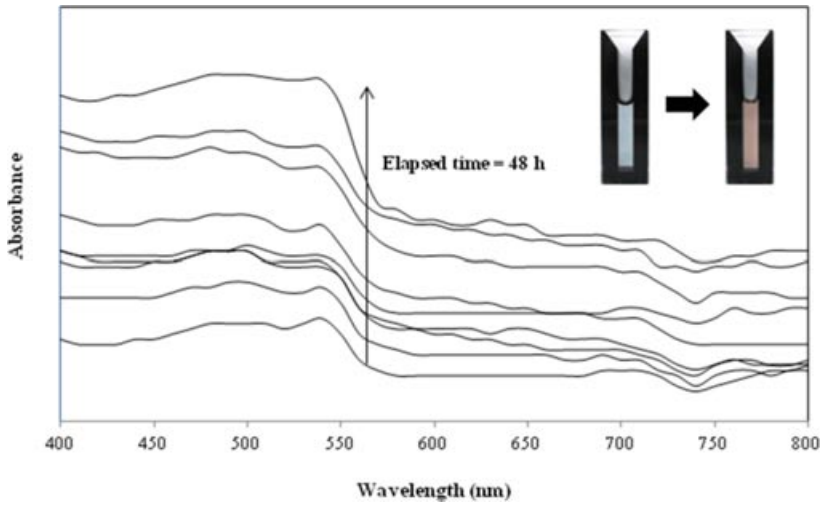

FIGURE 3. Absorption spectra and thermochromatic of PDA/silica nanocomposites with the concentration of Pluronic F127 of 15% w/v at 50°C and different storage time.

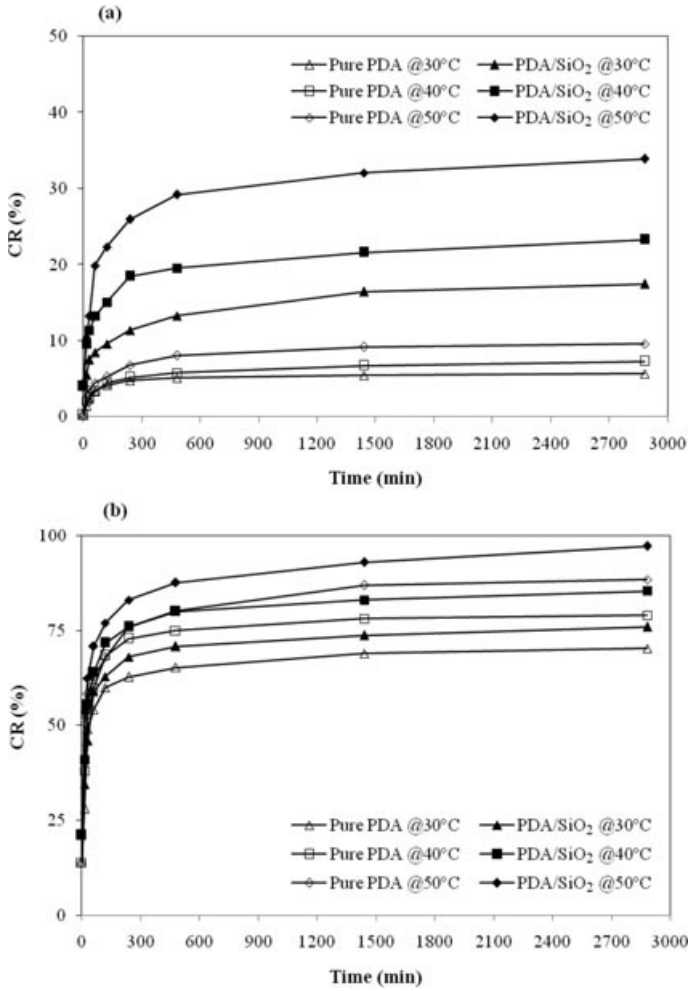

FIGURE 4. Color response of PDA/silica nanocomposites and pure PDA vesicles at the concentration of Pluronic F127 of 0% w/v (a) and 15% w/v (b), respectively, at different temperatures and time.

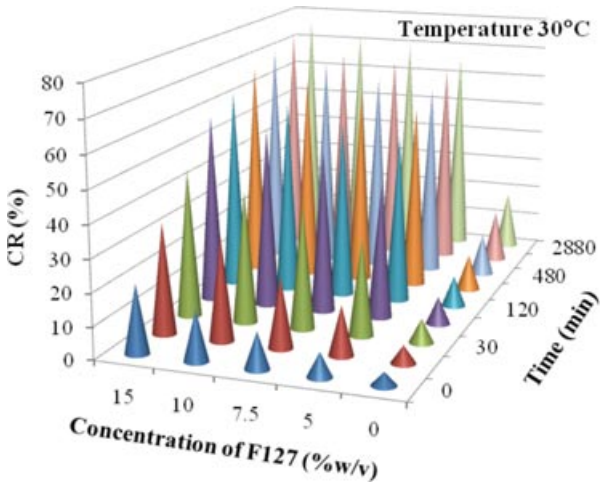

FIGURE 5. Color response of PDA/silica nanocomposites at the concentration of Pluronic F127 varying from 0 to 15% w/v at different times but at constant temperature (30°C).

in a range of 0–17% (Fig. 4a) and 0–80% (Fig. 4b), respectively, whereas the CR at 0 and 15% w/v Pluronic F127 without silica nanoparticles was in a range of 0–6% (Fig. 4a) and 0–70% (Fig. 4b), respectively. Moreover, the temperature can affect the color transition time of the PDA/silica nanocomposites. Higher temperature was observed with higher CR and faster color change.

Although the concentration of 0% w/v Pluronic F127 consisted of PEG400 only, the CR can slightly change the color as compared with the concentration of 5–15% w/v Pluronic F127. When the temperature was constant, the higher concentration of Pluronic F127 and time resulted in higher CR as shown in Fig. 5; whereas the higher concentration and temperature of Pluronic F127 resulted in higher CR when the time was constant. Therefore, all parameters such as the concentration of Pluronic F127, temperature, and time affected the color transition of the PDA/silica nanocomposites solution from blue to red.

Conclusions

This simple method can be used to prepare silica nanocomposites in the core shell of PDA vesicles, which increases color stability and intensity when exposed to UV light. However, we are careful about the stability of PDA vesicles as a result of its photooxidation, so the PDA/silica nanocomposites can be prepared without light. The color transition of the PDA/silica nanocomposites was an irreversible reaction and visible with the naked eye. At 5 wt% of the silica concentration, the absorbance of PDA/silica nanocomposites was higher than pure PDA vesicles and the color transition from blue to red was clearly visible. Finally, this study can be potentially developed as a new colorimetric polymeric indicator to study the effect of time and temperature on PDA/silica nanocomposites.

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