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Effect of cationic surfactants on characteristics and colorimetric behavior of polydiacetylene/silica nanocomposite as time–temperature indicator

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ABSTRACT

Polydiacetylene (PDA)/silica nanocomposites were synthesized by self-assembly method using polymerizable amphiphilic diacetylene monomers, 10,12-pentacosadiynoic acid (PCDA). Addition of cationic surfactants (PDADMAC and CTAB) to PDA/SiO_2 nanocomposites induced higher intermolecular force which affected their size, shape and color transition. Pure PDA, PDA/SiO_2, PDA/SiO_2/PDADMAC and PDA/SiO_2/CTAB were investigated by particle size analysis, TEM, SEM, UV–vis spectroscopy and FT-IR. It was found that the PDA/SiO_2 nanocomposites exhibited slightly larger particle sizes than those of other samples. The PDA/SiO_2 nanocomposites with a core–shell structure were almost regarded as spherical-shaped particles. Cationic surfactants, especially CTAB, presumably affected the particle size and shape of PDA/SiO_2 nanocomposites due to the disruption of hydrogen bonding between PDA head group and ammonium group. The colorimetric response of both PDA/SiO_2/surfactant and surfactant-free PDA/SiO_2 aqueous solutions directly changed in relation to time and temperature; thus they were expected to be applied as a new polymer-based time–temperature indicator (TTI).

1. Introduction

Polydiacetylene (PDA) is a conjugated polymer which can be prepared from various kinds of diacetylene monomers by photopolymerization [1]. It has attracted much attention for interesting and useful optical properties that have formed the basis for detection of biological things [2–5]. The sensing applications of PDA materials are widely developed in many fields due to its environmentally sensitive optical characteristics. One of the most interesting diacetylene monomers used to prepare PDA vesicles is 10,12-pentacosadiynoic acid (PCDA). It can display an intense blue color with a maximum absorption wavelength at ca. 640 nm under UV irradiation and optimal condition [6–8]. The color transition of PDA can shift from blue to red (ca. 550 nm of maximum absorption wavelength) upon designated environmental stimulation [1,9–15]. Generally, the chemical structure of PCDA consists of non-polar hydrocarbon tail group and polar carboxylic head group. Color transition of PDA can be occurred by rotation about one of the C–C bonds in the π-conjugated PDA backbone. The backbone changes from planar to non-planar state because the change in conjunction length of the π bonds could shift the absorption spectrum from blue to red [8]. The advantages of adding nanoparticles into PDA vesicles used as polymer additives are lower loading requirements and lower cost when provide competition to traditional additives technologies [16]. Moreover, the nanoparticles enhance an increase in their strong ionic interaction with functional groups of polymer chain [17], especially, carboxylic groups of the PDAs. Examples of nanoparticles which are widely used as PDA/nanocomposite are a silica dioxide (SiO_2) [18–22], zinc oxide (ZnO) [23–26], titanium dioxide (TiO_2) [27–29], silver (Ag) [30–33], and gold (Au) [34,35]. Nowadays, PDA/nanocomposites based on silica nanoparticles have attracted great interest due to their properties of optical transparency, controllable sizes, chemical inertness, biocompatibility,

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abrasion resistance, electrical insulation, and thermal stability. Additionally, they are highly abundant and inexpensive.

For the polar head of PDAs, a hydrogen atom of carboxylic group can interact with a carbonyl oxygen atom of a neighboring carboxylic group to form hydrogen bond. After bonding, carboxylic group is regarded as a COO^- form of carbonyl group, or is called anionic group. For silica nanoparticle, its binding surface in aqueous solution can be represented by Si–OH, $Si–OH_2^+$ and SiO^- groups [19,20]. Cationic surfactants (CS) can be used to modify the surfaces of silica nanoparticles to promote the electrostatic attractions between anionic PDAs and their charged head groups. They are widely used as consumer products (such as disinfectant, fabric softeners, cosmetic formulations and antistatic agents) and in industrial applications (such as dispersing agents, corrosion inhibitors and asphalt emulsifiers) [36]. Normally, their structures consist of hydrophobic tail (as hydrocarbon chain) and hydrophilic head (as cationic group), which is mostly in a chloride salt form and has antibacterial effect as well. According to above reasons, we were interested to focus on the addition of cationic surfactant to PDA/SiO_2 nanocomposites. The objectives of this present work were (i) to investigate the position of SiO_2 nanoparticles in PDA vesicles, (ii) to determine the effect of cationic surfactants on morphology of pure PDA and PDA/SiO_2 nanocomposites, and (iii) to assess the color change of all samples upon temperature and time.

2. Materials and methods

2.1. Materials

Most chemical reagents were commercially available, such as chloroform (Wako Pure Chemical Industries Ltd., Japan), poly(diallyldimethylammonium chloride) (PDADMAC) used as low molecular weight (Aldrich Chemical Co., Inc., USA), hexadecyltrimethylammonium bromide (CTAB) as powder (Tokyo Chemical Industry Co., Ltd., Japan) and MilliQ water. 10,12-pentacosadiynoic acid (PCDA) and Pluronic F127 were purchased from Aldrich (USA) and Sigma (USA), respectively. Poly(ethylene glycol)-400 (PEG-400, MW = 400) was supported by Siam Chemical Industry Co., Ltd. (Thailand). Also, untreated silica nanopowders (Trade name; Aerosil®200) which have a particle size in range of 12–40 nm are commercially available and provided by National Metal and Materials Technology Center (Thailand).

2.2. Preparation of PDA/silica nanocomposites in surfactant solution

10,12-Pentacosadiynoic acid (PCDA) monomer was dissolved in chloroform in a round bottom flask. The chloroform solution was removed by using a rotating evaporator until lipid layer was formed. Next, the cationic surfactant was dissolved in MilliQ water and its concentrations were varied at 0.0005%, 0.005% and 0.05%. Selected cationic surfactants were low molecular weight poly(diallyldimethyl ammonium chloride) (PDADMAC, $MW = 1.0–2.0 \times 10^5$) and cetyltrimethyl ammonium bromide (CTAB). Five percent by weight of silica concentration were dispersed in each surfactant solution by ultrasonic technique. After that, the suspension was added into the purified PCDA monomer and adjusted to be about 1 mM. The lipid suspension was ultrasonicated by a sonicator bath at 50 °C for 30 min. Next, the solution was cooled and stored overnight at 4 °C to induce crystallization of lipid membrane. After that, the solution was irradiated by UV-light at 254 nm for 5 min to yield a blue solution of polydiacetylene vesicle. At last, it should be stored at 4 °C or in a refrigerator until used.

2.3. Characterization of PDA solution

The morphology of PDA solutions (pure PDA, PDA/SiO_2 and PDA/SiO_2/surfactant) was investigated by using a transmission electron microscope (TEM, JEM-1010, JEOL, Japan) and a scanning electron microscope (SEM, JSM-5600LV, JEOL, Japan). The size distribution of particles was measured by a nanoparticle analyzer (SZ-100, Nano Partica Horiba Scientific, Japan). Samples for TEM and SEM measurements were prepared by dropping aqueous suspensions of these materials on TEM Cu grid and polished mica wafer, respectively. Using nylon syringe filter (0.45 μm pore size), it was to eliminate the contaminant from PDA solution. The solution was ultra-sonicated by sonicator bath prior to particle size distribution analysis which each sample was tested at 4 °C. The FT-IR spectra of samples were recorded in a TR mode at a resolution of $4\,cm^{-1}$ over a wavenumber range of $4000–400\,cm^{-1}$ (Tensor 27, Bruker, Germany). Before testing, samples were freeze-dried and prepared by KBr disc technique.

2.4. Preparation of PDA solution in amphiphilic polymer aqueous solution

Afterward, 0.1 mL of PDA solution (pure PDA, PDA/SiO_2 and PDA/SiO_2/surfactant) was mixed into 0.9 mL of the mixture between Pluronic F127 and PEG-400 as amphiphilic polymer aqueous solution. The concentration of F127 was varied from 0, 7.5 and 15% w/v. Then, the mixed solution was placed in a water bath at different temperatures (30–50 °C). The color of PDA/SiO_2 with surfactant was observed as compared with pure PDA and PDA/SiO_2 aqueous solution.

2.5. Color response measurement of PDA solution

The aqueous suspension was taken in a quartz cuvette. The absorption spectra were measured by using a UV–vis spectrophotometer (Model U-3000, Hitachi, Japan). After that, the absorbance at 640 and 540 nm were observed under room temperature and calculated to find the color response. The mathematical formula of color response (%CR) and percent blue (PB) are given by

$$\%CR = \left[\frac{(PB_0 - PB_1)}{PB_0}\right] \times 100 \qquad (1)$$

$$PB = \frac{A_{blue}}{(A_{blue} + A_{red})} \qquad (2)$$

when A is the absorbance at either the blue component (640 nm) or the red component (540 nm) of spectrum. PB_0 is the control, blue-ratio of pure PDA solution at the initial temperature, while PB_1 is the value of sample exposed to different temperature for different time.

3. Results and discussion

Normally, the color of PCDA changes from colorless to blue under UV light at maximum wavelength 254 nm. From the study of Nopwinyuwong et al. [19], the 5 wt.% of silica was added into PCDA without surfactant, which was colored blue after UV irradiation. However, with surfactant, it was found that the color of PDA/SiO_2/PDADMAC and PDA/SiO_2/CTAB were light blue which exhibited less intensity as compared to pure PDA and PDA/SiO_2. For the addition of amphiphilic polymer, the color of PDA/F127 solution changed from blue to red after it was exposed to different temperature and time, corresponding to the results reported by Nopwinyuwong et al. (Fig. 1) [37]. Its hydrophobic segments could be gradually inserted in the lipid monolayer of the PDA vesicles, which were mixed between F127 and PEG-400 to form poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) copolymer.