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A simple and inexpensive thermal optic nanosensor formed by triblock copolymer and polydiacetylene mixture

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ABSTRACT

Polydiacetylene (PDA) vesicles have been applied as optical sensors in different areas, although there are difficulties in controlling their responses. In this study, we prepared nanoblends of PDA with triblock copolymers (TC) as a better sensor system for detecting temperature change. The influences of diacetylene (DA) monomer, and the TC chemical structure and concentration on the colorimetric response (CR) were examined. The TC/PDA nanoblend was remarkably more sensitive to temperature change, than classical vesicles. A higher L64 concentration of 12.0% (w/w) reduced the chromatic transition temperature (T_{tr}) to as low as 24 °C. When using different TCs, the T_{tr} values can be ordered as L35 < F68 < L64 < F127 < P123, indicating the importance of the hydrophobic environment for the colorimetric transition of nanoblends. The results here demonstrated that the balance of intermolecular interaction between TC-TC, TC-DA, and DA-DA enables the construction of strategic sensor for detecting temperature changes in different applications.

1. Introduction

Temperature change detection is important for numerous industrial applications, such as the storage and transport of food, medicine and cosmetics, as well as chemical reaction control. To obtain simple, inexpensive and customizable response sensors for temperature change is key to guaranteeing the quality assurance of different formulations. The polydiacetylene (PDA)-based optic sensor has emerged as a promising solution for this purpose. PDA is formed by ene-yne conjugated polymers through the 1,4-addition of diacetylene monomers, which, when properly oriented, polymerize in several self-assembled forms, such as monolayer, multilayer, nanostructured particles, micelles and vesicles (Baek, Song, Lee, & Kim, 2016; Shin & Kim, 2016; Wen, Bohorquez, & Tsutsui, 2016).

The PDAs have the interesting chromatic ability of changing from blue to red in colour under various stimuli, such as temperature (Guo et al., 2016), pH (Seo et al., 2013), and the presence of various surfactants (Shin, Shin, & Shin, 2017; Zhang et al., 2017), organic solvents (Pires et al., 2010), proteins (De Souza et al., 2016; De Paula et al., 2017) and some viruses and bacteria (Pires et al., 2011). A large number of studies have explored the chromatic properties of PDAs to develop smart sensors (Kamphan, Charoenthai, & Traiphol, 2016; Kamphan, Khanantong, Traiphol, & Traiphol, 2017; Yang et al., 2016). However, the modulation of the stimulus range is particularly difficult for developing and implementing PDA-based sensors (Shin, Byun, & Kim, 2015). In general, to achieve a complete blue-red transition, the applied stimulus is restricted to a very specific and small range. For example, vesicles prepared with polymerization of 10,12-pentacosadiynoic acid (PCDA) monomers undergo a gradual colorimetric transition with increasing temperature. However, the absorption spectrum and the colour of the material do not display abrupt change until 55 °C, and the material is completely converted from blue to red at ~60–70 °C (Chen & Yoon, 2011; Kamphan et al., 2016). Therefore, modulating and extending the range of the colorimetric transition in PDAs without modifying the diacetylene structure is of great scientific and technological importance.

The EO-PO-EO (EO = ethylene oxide, PO = propylene oxide) triblock copolymers, commercially known as Pluronics or Synperonics,

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are amphiphilic molecules capable of self-aggregation in aqueous solutions to form micelles. Such a micelle has a hydrophobic core composed mainly of PO segments, and a hydrophilic shell formed by repeated EO units (Liu & Li, 2015; Nagarajan, 1999). Thus, the copolymers provide a suitable template in aqueous solutions for the insertion and orientation of diacetylene monomers in the hydrophobic core of the aggregates, which act as special reactors for the polymerization process (De Souza et al., 2016; De Paula et al., 2017). De Souza et al. (2016) and De Paula et al. (2017) used the nanostructured PDA-triblock copolymer L64 blend to detect milk proteins, such as micellar casein and bovine serum albumin. In addition, the chemical structure of the copolymer in these blends may affect the resulting sensor sensitivity, because the sizes of aggregates and hydrophobic core depend on the concentration, molecular weight, and the EO/PO ratio of the macromolecules (Kulthe et al., 2011).

Inspired by these results, we synthesized two different PDAs using PCDA or 10,12-trycosadyinoic acid (TCDA) polymerization in amphiphilic environments formed by distinct copolymers. The effects of the hydrophobic/hydrophilic balance, molecular weight, and concentration of the copolymer on the PDA's chromatic transition upon temperature change (thermochromism) were investigated.

2. Material and methods

2.1. Materials

PCDA, TCDA, and the triblock copolymers L35, L64, F68, P123, and F127 were purchased from Sigma-Aldrich (USA). All chemicals were used without further purification. Milli-Q® water (EMD Millipore, Billerica, MA, USA) was used for the preparation of all solutions.

2.2. Vesicle and blend preparation

To prepare classical PDA vesicles, PCDA monomers were dissolved in $CHCl_3$, and the solvent was then removed by a stream of N_2 gas. Deionized water was added to adjust the total lipid concentration to 1 mM. The resulting system was sonicated to obtain a clear solution, which was immediately filtered using a 0.45-µm PVDF filter (Merck Millipore Ltd, Ireland). The resulting suspension was stored at 4 °C for 12 h to induce crystallization of the lipid membranes. Polymerization was then carried out under irradiation at 254 nm wavelength for 5 min (Pires et al., 2010).

For the construction of PDA/TC nanoblends, PCDA or TCDA was dissolved in the copolymer aqueous solution of different concentrations without any pre-treatment. The mixture was sonicated for 10 min, filtered through a 0.45-µm PVDF filter (Merck Millipore Ltd, Ireland), and then kept at 4 °C for 12 h. The subsequent PCDA or TCDA polymerization process was carried out in the same way as for the vesicles (De Souza et al., 2016; Ortega, 2013).

2.3. Quantifying the colorimetric response

To analyze the effect of temperature on PDA vesicles and nanoblends, 0.7 µl of the sample was added into the UV–visible cell with the temperature controlled by a Peltier system (Shimadzu TCC-240 A, Shimadzu Scientific Instruments, Columbia, MD, USA) at fixed values between 15 and 70 °C. The UV spectra were obtained between 350 and 900 nm (Shimadzu UV-2550, Shimadzu Scientific Instruments, Columbia, MD, USA) after achieving thermal equilibrium. To quantify the extent of blue-to-red colour transition, the colorimetric response (CR, %) was calculated using the following equation:

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

where PB = $A_{blue}/(A_{blue} + A_{red})$, with A being the absorbance at blue (~650 nm) or red (~540 nm) obtained by UV–vis spectroscopy. PB_0 is the control value of PDA nanoaggregate (vesicle or nanoblend) at 15 °C, while PB_1 is that of the sample at another temperature.

2.4. Measurements of nanoaggregate size and zeta potential of nanoblends

The size (hydrodynamic diameter) and zeta potential of nanoblends were measured with a Zetasizer nano ZS90 (Malvern, UK) system at 25 °C. Samples were diluted by a factor of 20, so that their blue colour would not interfere with the laser used for measurements. Each measurement was repeated 3 times, and each reported result was the average of 10 measurements.

3. Results and discussion

The synthesis of classical PDA vesicles uses organic solvents and is often a complex process. To overcome these limitations, a simple and fast method based on the solubilization of DA monomers (PCDA or TCDA) in a triblock copolymer solution had been proposed.

To evaluate the potential application of poly-PCDA (PPCDA)/copolymer nanoblends as thermic nanosensors, their temperature-dependent optical properties were analyzed. Moreover, to determine the optical response to temperature of PPCDA inside these new nanoaggregates (nanoblends), the UV–vis spectra were obtained and compared with those of classical PPCDA vesicles at two different temperatures (25.0 °C where the colour is blue and 60 °C when the material turns red). Fig. 1 shows the spectra of PPCDA vesicles and PPCDA/L64 nanoblends at both temperatures. In each sample, the diacetylene monomer concentration in the nanostructure was 1.0 mM, the L64 concentration was 1.0% (w/w), and the sample was diluted from the as-synthesized solution with solvent of synthesis by a factor of 10.

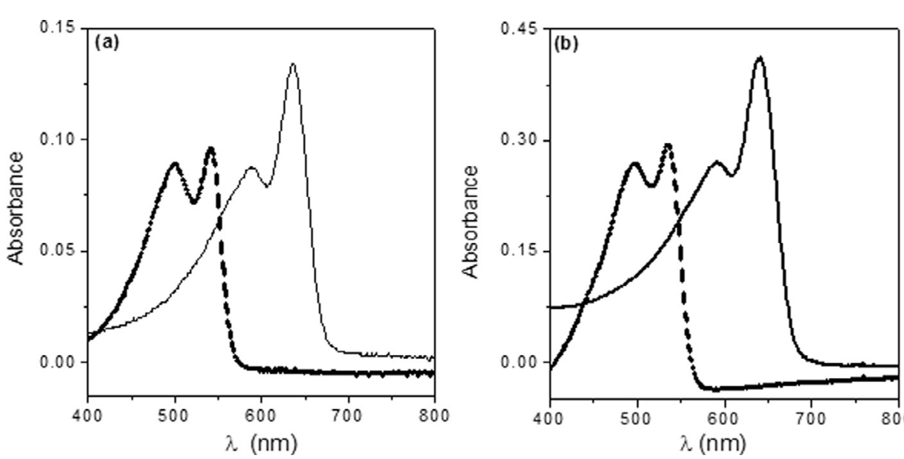

Fig. 1. UV–vis absorption spectra of (a) PPCDA vesicle solution and (b) PPCDA/L64 nanoblends solution at 25 °C (solid line) and 60 °C (dashed line).