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Influences of structural mismatch on morphology, phase transition temperature, segmental dynamics and color-transition behaviors of polydiacetylene vesicles

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ABSTRACT

In this contribution, we report a systematic study of polydiacetylene (PDA) vesicles fabricated by mixing two types of monomers, 10,12-tricosadiynoic acid (TCDA) and 10,12-pentacosadiynoic acid (PCDA). These diacetylene (DA) monomers constitute the same head group but different alkyl chain length, which in turn causes structural mismatch within the PDA layers. The PCDA:TCDA ratios are 100, 75, 50, 25 and 0 mol%. Morphologies and properties of these PDA vesicles are explored by utilizing laser light scattering, transmission electron microscopy, differential scanning calorimetry, temperature-dependent nuclear magnetic resonance spectroscopy (NMR) and spin–lattice relaxation time (T_1) measurements. An increase in DA mole ratio to 50 mol% leads to significant increase in particle size. The mixed PDA vesicles also exhibit irregular shape with rather rough surface. The mismatch of alkyl side chain causes the drop of phase transition temperature. For the system of mixed poly(PCDA50:TCDA50), its transition temperature is lower than those of the pure PDAs. The NMR line shape analysis detects an abrupt change of proton signal adjacent to the PDA head group during the blue/red color-transition process. The T_1 measurements also reveal different local environments of PDA alkyl side chains in the blue and red phases. The mismatch of PDA side chains causes significant drop of the color-transition temperature.

1. Introduction

Polydiacetylene (PDA) vesicles are conjugated polymers that have received considerable attention as colorimetric sensing materials due to their visual color transitions after exposure to external stimuli such as temperature [1–9], acids and bases [10–16], ions [17–20], and organic solvents [21–25]. In general, the color transition of PDA vesicles results from the rearrangement of their segments caused by the variation of local environments [9,10,26–30]. The change of chain conformation and segmental packing causes the decrease of effective conjugation length of the PDA backbone, which in turn leads to drastic blue shift of absorption spectrum. Unperturbed PDAs normally show a blue color whereas perturbed systems can exhibit purple, red and orange colors, depending on the magnitude of segmental rearrangement.

The colorimetric response of PDAs to external stimuli has been investigated by many research groups. The main goal of these works normally seeks for the ability to control the color-transition property of PDA. Many researchers have synthesized new classes of PDAs constituting various types of head groups and side chains [1,5,8,11–15]. It has been demonstrated that the colorimetric response of these newly synthesized PDAs to external stimuli can be systematically controlled by using different synthetic approaches. However, the synthesis is normally a multistep method and also requires time-consuming purification processes, which are major disadvantages for large scale production. Therefore, some recent works introduce alternative approaches by using additives. For example, the incorporation of ZnO nanoparticles into PDA systems results in reversible thermochromism [6,7,16]. The use of Zn^{2+} and Na^{+} ions as additives also provides similar result [9,28,31]. In addition, the reversible color-transition temperature of these PDAs can be controlled by varying the length of alkyl side chain.

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The fabrication of PDAs by using two types of diacetylene (DA) monomers is a facile method for fine tuning the color-transition properties [18,19,32–40]. This approach is normally utilized when PDAs are used to sense some biomolecules such as sugar, antibody and virus [32,37–40]. In this system, the head groups of some PDAs are functionalized with specific moieties. Similar mixing approach is also utilized to develop PDAs for sensing various chemicals such as warfare gases [35], K^+ ion [19], Hg^{2+} ion [18] and volatile organic solvents [34,36]. Furthermore, You et al. demonstrate that color transition of PDA can occur upon exposure to UV–vis light when some head groups are functionalized with azobenzene moiety [41]. However, most of these works mainly focus on the color-transition properties while the segmental organization within the mixed PDA vesicles is hardly investigated. The mixing of DA monomers with slight difference of their chemical structures may result in significant change of segmental packing within the PDA vesicles.

In this contribution, we extensively investigate the effects of alkyl side chain mismatch of PDAs on the morphology and colorimetric response to temperature. The PDA vesicles are fabricated by mixing 10,12-pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid (TCDA) monomers. These DA monomers have slight difference of the alkyl chain length while the head groups are the same (see Fig. 1). The difference of alkyl chain length may cause defects within the bilayer structure and hence reduces inter/intra-chain dispersion interaction. In this study, the transition temperature and segmental dynamics of mixed PDAs are followed by using different techniques. The colorimetric response of mixed PDAs to temperature is investigated. We observe that the slight difference of side chain mismatch leads to significant change of the color-transition behaviors.

2. Materials and methods

The PCDA and TCDA monomers were purchased from Fluka. The preparation of PDA vesicles was described in our previous studies [15,24]. The mole ratios of PCDA:TCDA were varied as 100:0, 75:25, 50:50, 25:75 and 0:100 mol%. These DA monomers were mixed during the preparation process prior to the polymerization. Size distribution and morphologies of the mixed PDA vesicles were investigated by laser light scattering (Malvern Mastersizer 2000) and transmission electron microscopy (TEM, Tecnai 12, D291), respectively. Samples for TEM measurements were prepared by drop-casting from PDA suspensions onto copper grids coated with carbon film. Thermal properties of each mixed vesicle were investigated by using differential scanning calorimetry (DSC) (Mettler Toledo DSC1). We could not measure DSC trace directly from the PDA aqueous suspensions because their concentrations were extremely low (0.5 mM). Therefore, all PDA vesicles were dried at room temperature and left in vacuum oven for one night prior to the DSC measurement. About 3–5 mg of dried sample was encapsulated in aluminum pan and measured under nitrogen gas, using 5 °C/min heating and cooling rate. The melting point was measured at peak temperature.

The temperature-dependent ^1H NMR measurements of PDAs were carried out by a Bruker Avance-400 at 400 MHz. The PDA solutions for NMR measurements were prepared in deuterium oxide (99.9%, Sigma–Aldrich). The NMR instrument was equipped with a variation temperature unit, which can control temperature to ±0.1 °C. The temperature was calibrated by using a solution of 80% 1,2-ethane-diol in $DMSO_{-d6}$. Single pulse with $\pi/2 = 7.8\ \mu s$ and a delay time of 5 s was used. Spin–lattice relaxation time (T_1) measurements were carried out using π-τ-$\pi/2$-(FID detection) sequence. The T_1 of PDAs in blue and red phases was measured from the same sample. The red phase was obtained by raising the temperature to about 60 °C. Absorption spectra of mixed PDAs were measured by using UV–vis spectrometer (Analytik Jena Specord S100) equipped with diode array detector and variable-temperature sample holder. To quantify the extent of blue to red color-transition of PDAs, the colorimetric response or CR(%) was calculated as described in our previous reports [15,24].

3. Result and discussion

3.1. Size distribution and morphology

The fabrication of PDA vesicles by using mixtures of PCDA and TCDA monomers results in the increase of particle size as shown in Fig. 2. The pure poly(PCDA) and poly(TCDA) vesicles exhibit median diameter of about 60 nm with relatively narrow size distribution. The presence of 25 mol% TCDA within the PDA vesicles

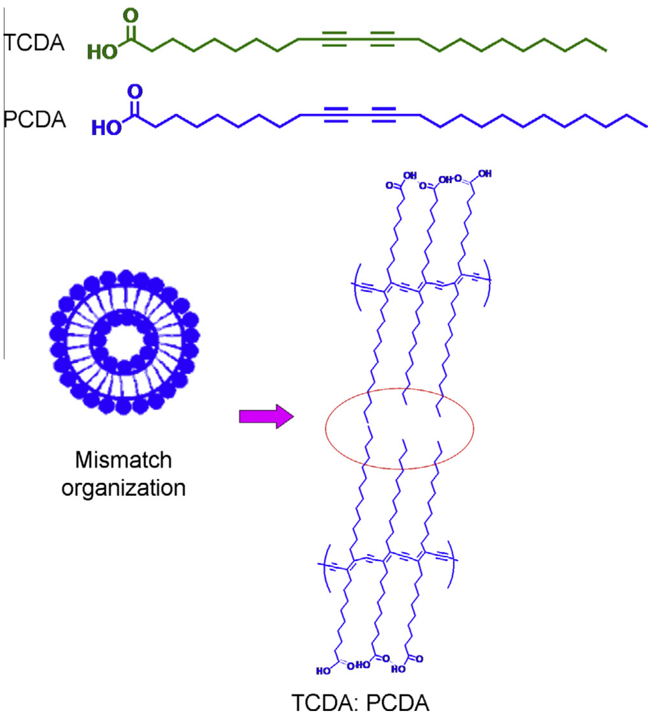

Fig. 1. (above) Chemical structure of diacetylene monomers, 10,12-tricosadiynoic acid (TCDA) and 10,12-pentacosadiynoic acid (PCDA). (below) Structure of polydiacetylene vesicle and the mismatch in the packing of alkyl side chains.

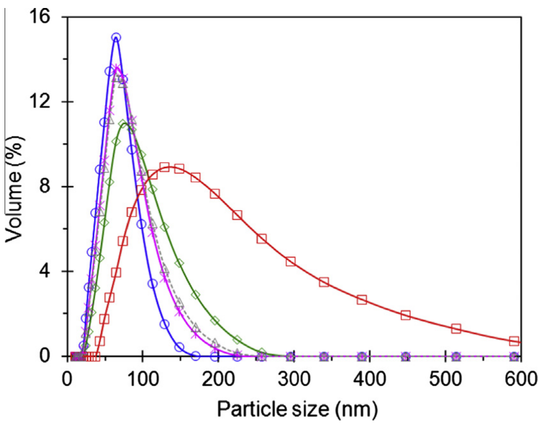

Fig. 2. Particle size distribution of PDA vesicles in aqueous suspension. Symbols are for (△) poly(TCDA), (×) poly(TCDA75:PCDA25), (□) poly(TCDA50:PCDA50), (◇) poly(TCDA25:PCDA75) and (○) poly(PCDA) vesicles.