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Concentration and temperature-sensitive assembling behavior of polyethyleneimine–cinnamic acid conjugate and its release-controlling property in monoolein cubic phase

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ABSTRACT

Temperature-responsive monoolein (MO) cubic phase was prepared by including polyethyleneimine (PEI) and cinnamic acid (CA) in the cubic phase. PEI/CA aqueous solution exhibited reversible upper critical solution temperature (UCST) behavior. CA and PEI was included in the cubic phase so that the concentrations were the same as those in PEI/CA solution which exhibited reversible UCST behavior from 32 °C to 50 °C. The maximum release degree of methylene blue observed above UCST (12.5% at 45 °C and 13.1% at 50 °C) was apparently higher than the maximum release degree below UCST (4.1% at 25 °C and 4.3% at 30 °C).

Introduction

Monoolein (MO) can constitute bicontinuous cubic phase in aqueous phase because it is an amphiphiles whose packing parameter is slightly greater than 1 [1]. In MO cubic phase, two intercrossing water channels (about 5 nm in diameter) are surrounded by the lipidic matrix of MO bilayers (about 3.5 nm in thickness). Since the cubic phase is isotropic, it is optically transparent. The amount of water MO cubic phase can imbibe is 28% to 40%, and the cubic phase is classified into gyroid type and diamond type, depending on the water content. Since the cubic phase has water channels and lipidic matrix, it can accommodate both water-soluble compounds and oil-soluble compounds. Recently, MO cubic phases which could promote or suppress the release of their payloads in response to stimuli such as temperature change [2,3], pH change [4–6], and light irradiation [7] were developed. Poly(*N*-isopropylacrylamide) (PNIPAM), a thermo-responsive polymer exhibiting a lower critical solution temperature (LCST), was immobilized in the water channel of MO cubic phase to obtain thermo-responsive controlled release. Below the LCST, the polymer chains take a stretched form and they could act as a resistance against the diffusion of a water-soluble compound. Above the LCST, the polymer chains take a contracted form and they could less hinder the diffusion [8]. Alginate and silk fibroin were together included in the water channel to develop a pH-responsive cubic phase [9]. At a low pH value, complex coacervate of two natural polymers were formed and it could hinder the diffusion of a solute in the water channel. As the pH value increased, the coacervate was dissolved and the diffusivity could increase [9]. Gold nanospheres were embedded in the lipidic matrix of MO cubic phase to obtain near infrared(NIR) irradiation-triggered release [3]. Due to the surface plasmon resonance under NIR irradiation, gold nanoparticle generated heat and the cubic phase could be subjected to the phase transition from cubic phase to reversed hexagonal phase, resulting in a promoted release. In this study, cinnamic acid (CA) and poly(ethyleneimine) (PEI) were included in MO cubic phase to develop a temperature-responsive cubic phase. PEI could be conjugated with CA through the electrostatic interaction between the amino group of PEI and the carboxylic group of CA. It was demonstrated in this study that PEI/CA conjugates could be self-assembled into gel particles and they exhibited reversible upper critical solution temperature (UCST) behavior in aqueous phase. Below UCST, PEI/CA conjugates could be assembled and they would suppress the diffusion of a

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diffusate through the water channels of MO cubic phase. When the temperature increased across UCST, the self-assembly (gel particles) was disintegrated and PEI/CA conjugates would hardly hinder the diffusion (Fig. 1).

Materials and methods

Chemicals

Monoolein (MO) was gifted from BASF Korea Ltd. (Seoul, Korea). Methylene blue, poly(ethylenimine) (PEI, MW 2000, branched form), trans-cinnamic acid (CA) and Trizma base were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). All other reagents were in analytical grade.

Temperature-dependent transmittance of PEI/CA mixture solution

PEI and CA were dissolved together in 5 ml of Trizma bases buffer (pH7.0) so that the molar ratio of the amino group of PEI to the carboxylic group of CA was 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9, respectively, and the total concentration of the amino group plus the carboxylic group was constant. To obtain those conditions, the concentration of PEI and that of CA were adjusted to 13.2 mg/ml/5 mg/ml, 11.8 mg/ml/10 mg/ml, 10.3 mg/ml/15 mg/ml, 8.8 mg/ml/20 mg/ml, 7.4 mg/ml/25 mg/ml, 5.9 mg/ml/30 mg/ml, 4.4 mg/ml/35 mg/ml. 2.9 mg/ml/40 mg/ml, and 1.5 mg/ml/45 mg/ml. (The ratio and the concentration were summarized in complementary data 1). The temperature-dependent transmittance of PEI/CA mixture solutions was determined by measuring the optical density of the mixture solution at 600 nm on a UV spectrophotometer (JENWAY

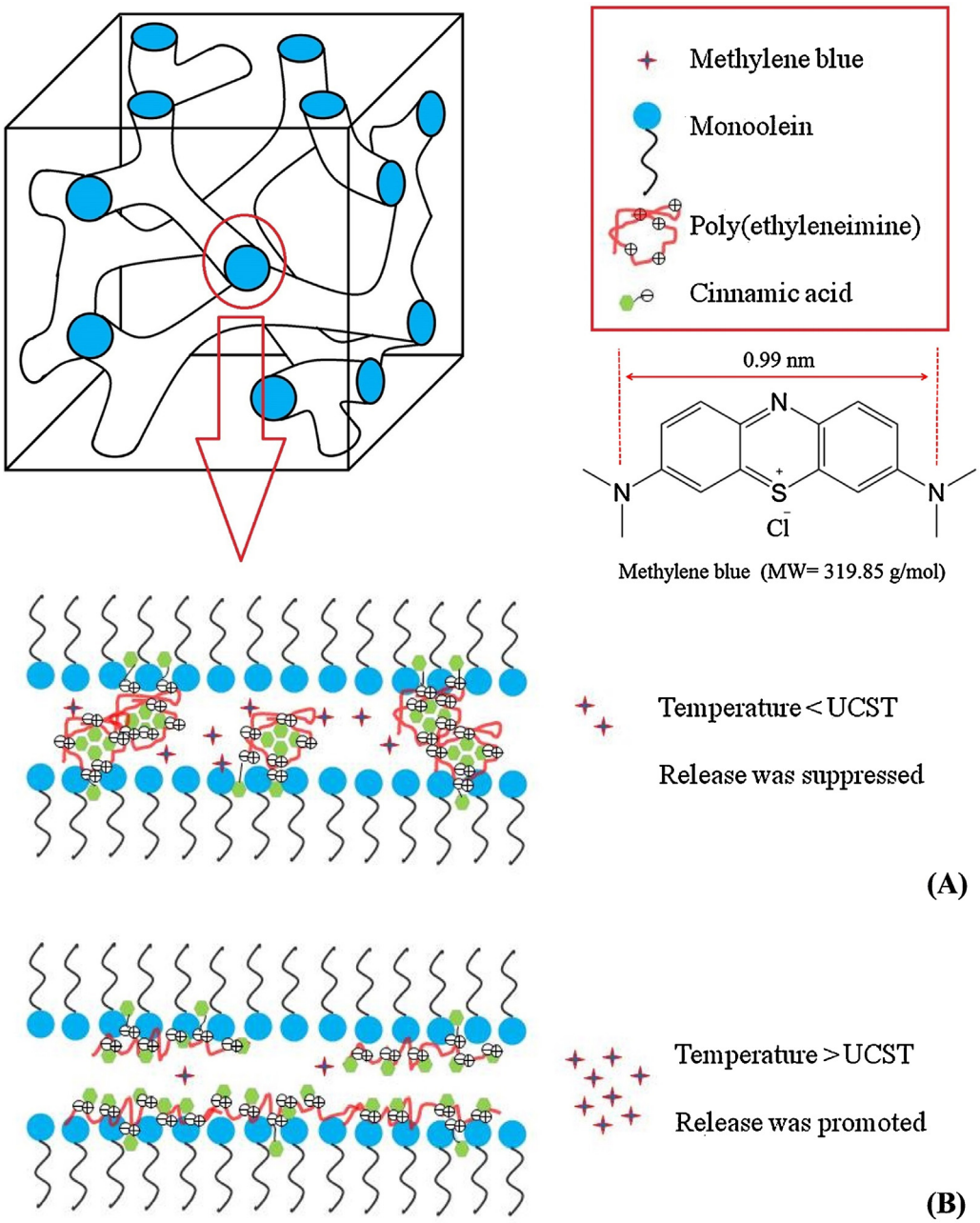

Fig. 1. Monoolein cubic phase containing PEI/CA conjugate. Below UCST, PEI/CA conjugates can be assembled and they would suppress the diffusion of a diffusate through the water channels of MO cubic phase (A). When temperature increases across UCST, the self-assembly (gel particles) will be disintegrated and PEI/CA conjugates would hardly hinder the diffusion (B).