



Complex micelle formation between poly(ethylene oxide-*b*-*N*-methyl-2-vinylpyridinium iodide) and poly(methacrylic acid) in aqueous solutions

Sudhina Guragain^a, Bishnu P. Bastakoti^a, Masatoshi Hasegawa^b, Kenichi Nakashima^{a,*}

^a Department of Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840-8502, Japan

^b Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

ARTICLE INFO

Article history:

Received 10 February 2010

Received in revised form 9 April 2010

Accepted 12 April 2010

Available online 18 April 2010

Keywords:

Nanocomplex

Poly(ethylene

oxide-*b*-*N*-methyl-2-vinylpyridinium

iodide)

Poly(methacrylic acid)

ABSTRACT

Complex micelles are prepared from poly(ethylene oxide-*b*-*N*-methyl-2-vinylpyridinium iodide) (PEO-*b*-P2VPQ), one of double-hydrophilic block copolymers, and poly(methacrylic acid) (PMAA) in aqueous solutions. The formation of the complex micelles is due to the insolubilization of the cationic P2VPQ block of PEO-*b*-P2VPQ with anionic PMAA. The complex micelles are characterized by various techniques including ζ -potential measurements, dynamic light scattering, fluorescence spectroscopy, and scanning electron microscopy. It is revealed that the micelles have spherical morphology with hydrodynamic diameter ranging from ca. 69 to 80 nm and that the hydrodynamic diameter depends on the conditions such as polymer concentration and ionic strength.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

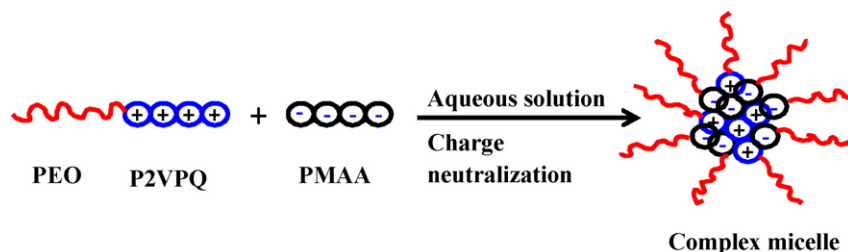
Increasing attention has been paid to the micellar complexes not only for their fascinating physicochemical properties but also for their potential applications in detergency, catalysis, nanoparticles synthesis, and drug delivery [1,2]. Recently, double-hydrophilic block copolymers (DHBCs) have attracted much attention among them. DHBCs are diblock copolymers consisting of two water soluble blocks with different chemical nature. Typical examples of DHBCs are poly(ethylene oxide-*b*-aspartic acid) and poly(ethylene oxide-*b*-methacrylic acid) (PEO-*b*-PMAA) [1,2]. They do not form micelles when dissolved in water. However, if one of the blocks is insolubilized with surfactants, metal ions, or some other chemicals, they form micelles with core of the insolubilized block and corona of the other block [1–4]. One of the features of DHBC assemblies is that ionic species can be incorporated into the core domain of the assemblies. Thus, DHBC assemblies can be used as a nanocarrier for ionic drugs and a nanoreactor for chemical reactions of ionic species. These functionalities cannot be realized in conventional micelles of amphiphilic polymers, which have a highly hydrophobic core. Therefore, DHBC assemblies are of considerable interest both in basic studies and applications.

Harada and Kataoka [5,6] succeeded in getting polyion complex micelles using poly(ethylene glycol-*b*-L-lysine) and poly(ethylene glycol-*b*- α,β -aspartic acid) in aqueous solutions. The electrostatic interaction between the polycation and polyanion blocks provided a driving force of micelle formation. Several groups [7–9] have reported the formation of aggregates between neutral-anionic DHBCs and metal ions. For example, Gérardin et al. [7] prepared hybrid micelles of poly(acrylic acid-*b*-hydroxyethylacrylate) and Al³⁺, and used the micelles as a precursor for the synthesis of highly stable metal hydrous oxide colloids. Our group [10–12] prepared block ionomer micelles by the binding of alkaline earth metal ions (Ba²⁺ and Ca²⁺), surfactants (cetyltrimethylammonium chloride), or polymer (poly-L-lysine) to PEO-*b*-PMAA.

Although there are a lot of studies on DHBC micelles, a combination of neutral-*b*-cationic type DHBC with anionic species is scarcely found [13,14] except for the systems containing DNAs for a gene delivery application. Wu et al. [15] studied complex micelles of poly(ethylene glycol-*b*-4-vinylpyridinium) cations (PEG-*b*-P4VPH⁺) and SO₄²⁻ ions. This system is one of a few examples of a combination of neutral-cationic DHBC and inorganic anions. The system shows interesting properties and promising applications in the delivery and manipulation of anionic species. They also studied thermo responsiveness of hybrid micelles from PEG-*b*-P4VPH⁺ cation and SO₄²⁻ anion in aqueous solutions [16]. Zhang et al. [17] studied comicellization of poly(ethylene glycol-*b*-acrylic acid) (PEG-*b*-PAA) and poly(4-vinylpyridine) P4VP in ethanol, and found

* Corresponding author.

E-mail address: nakashik@cc.saga-u.ac.jp (K. Nakashima).



Scheme 1. Pictorial representation of the structure of the complex micelle.

that the system results in micellar complexes with the hydrogen bonded PAA/P4VP as core and PEG as corona.

In this paper we have studied the formation of micelles of poly(ethylene oxide-*b*-*N*-methyl-2-vinylpyridinium iodide) (PEO-*b*-P2VPQ) using PMAA as counter ion. This system seems to have considerable potential applications, because it can be employed as nanoreactors for fabrication of organic and inorganic nanoparticles as well as it can be regarded as a model of block-copolymer-based nanocarriers for anionic polymeric medicines. Addition of PMAA into aqueous solution of PEO-*b*-P2VPQ results in the formation of micelles with P2VPQ/PMAA mixed core and PEO neat corona as a result of charge neutralization of quaternized P2VPQ with anionic PMAA (Scheme 1). The complex micelle has been characterized using dynamic light scattering (DLS), ζ -potential measurement and scanning electron microscopy (SEM). Fluorescence measurement was also carried out to know the micro-viscosity inside the micelle as well as to confirm the binding of PMAA to PEO-*b*-P2VPQ.

2. Materials and methods

2.1. Materials

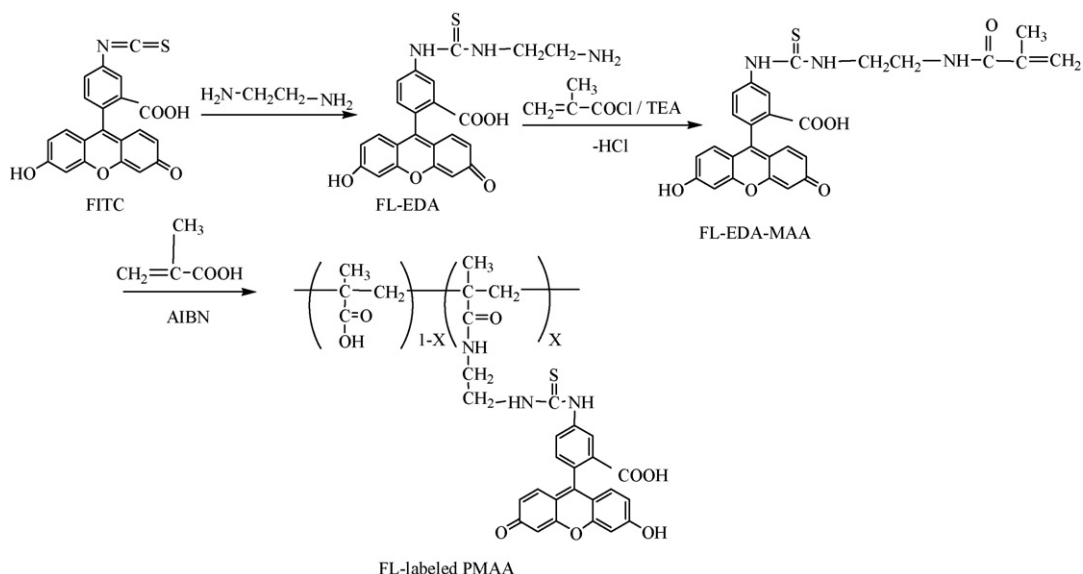
PEO-*b*-P2VPQ diblock copolymer (Polymer Source Inc.) and PMAA homopolymer (Polysciences Inc.) were used as supplied. The molecular weights are $M_n = 5900$ for PEO and $M_n = 56,500$ for P2VPQ in PEO-*b*-P2VPQ. According to the supplier, the degree of quaternization of the P2VPQ block is 86%. The molecular weight of PMAA homopolymer is 15,000. Phosphate buffered saline (PBS) (pH 7.4) was purchased from Lonza.

2.2. Synthesis of fluorescein-labeled PMAA

Fluorescein-labeled PMAA (FL-PMAA) was prepared according to a previous report [18]. The reaction scheme is shown in Scheme 2. A large excess of ethylenediamine (EDA, 17.0 mmol) was dissolved in 3 mL anhydrous tetrahydrofuran (THF) in a 100 mL flask. To this solution, a THF solution (10 mL) containing 1.0 mmol fluorescein isothiocyanate (FITC, Wako Pure chemical Industries) was slowly added at room temperature. Then, the solution was stirred for 3 h at room temperature. After the solvent was removed in an evaporator, the product was vacuum-dried at 70 °C for 12 h to ensure complete removal of unreacted EDA. The orange-colored product was recrystallized from methanol.

The purified FL-EDA (0.89 mmol) was dissolved in 20 mL anhydrous dimethylsulfoxide (DMSO) and triethylamine (17 mmol) as an acid acceptor. To this solution, methacryloyl chloride (MAC, 9.6 mmol, Tokyo Chemical Industry, stabilized with methoxyhydroquinone (MEHQ)) was added, and then the solution was stirred at room temperature for 12 h. After removal of triethylamine-hydrochloride salt by filtration, the filtrate was slowly dropped in a large amount of ether to form precipitate. The precipitate was repeatedly washed with ether to ensure complete removal of unreacted MAC and MEHQ.

The product (FL-EDA-MAA) was used for copolymerization with methacrylic acid (MAA, Wako Pure Chemical Industries). MAA was dissolved in methanol in a 100 mL three-necked flask equipped with a nitrogen inlet, a thermometer, and a condenser. To this solution, an established amount of FL-EDA-MAA dissolved in a methanol (22 mL)/DMSO (3 mL) mixed solvent and azobisisobutyronitrile (AIBN) as an initiator were added at room temperature. The



Scheme 2. Reaction scheme of FL-labeled PMAA preparation.

Download English Version:

<https://daneshyari.com/en/article/595373>

Download Persian Version:

<https://daneshyari.com/article/595373>

[Daneshyari.com](https://daneshyari.com)