



Surface-tunable colloidal particles stabilized by mono-tethered single-chain nanoparticles



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ABSTRACT

In these years synthesis and applications of single-chain nanoparticles (SCNPs) have aroused great interests. In this article, the surfactant behaviors of amphiphilic mono-tethered SCNPs are reported. Amphiphilic mono-tethered SCNPs were prepared by intramolecular cross-linking reaction. In the mono-tethered SCNPs, there are disulfide bonds at the junction points between coil chains and the SCNPs. ¹H NMR, size exclusion chromatography and transmission electron microscopy results demonstrated successful synthesis of the SCNPs. The amphiphilic mono-tethered SCNPs are able to lower the surface tension of water. Critical micelle concentration of the SCNPs in aqueous solution was determined. The mono-tethered SCNPs were used as surfactants in the suspension polymerization of styrene, and polystyrene colloidal particles with SCNPs on the surfaces were prepared. SCNPs on the colloidal particles were cleaved from the surfaces of the colloidal particles, leaving thiol groups on the surfaces. Pyridyl disulfide-modified PS colloidal particles were synthesized by a reaction between 2,2'-dipyridyl disulfide and the thiol groups on the PS particles. The pyridyl disulfide-modified colloidal particles were used as a platform for the preparation of functional colloidal particles. Herein, fluorescence-labeled colloidal particles were prepared by a reaction of thiol-modified fluorescein isothiocyanate and pyridyl disulfide groups on the particles.

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1. Introduction

Surfactant molecules are the compounds that lower the surface tension or interfacial tension between liquid and air or between liquid and liquid [1]. Small-molecule surfactants consisting of a hydrocarbon tail and an ionic head, have found wide applications in industry and daily life. Similar to the small-molecule surfactants, amphiphilic block copolymers or graft copolymers are also used as surfactants [2]. Polymeric surfactants have many interesting properties, such as low critical micelle concentration (CMC) and low mobility.

Solid particles in an emulsion undergo self-assembly onto liquid–liquid or liquid–air interfaces, and the emulsion is referred to as a Pickering emulsion [3]. Solid particles with different chemical properties and different sizes have been used as solid surfactants in the fabrication of new hybrid materials [4]. Among the solid particles, the particles with asymmetric structures have strong

tendency to locate at surfaces or interfaces. For example, amphiphilic Janus particles are able to undergo interface-directed self-assembly at the water–oil interface with the hydrophobic hemispheres immersed in the oil phase and the hydrophilic hemispheres in the aqueous phase [5]. The amphiphilic Janus particles are efficient surfactants in the emulsion polymerizations [6]. With the rapid development of nanoscience and polymer synthesis, many different polymer-tethered nanoobjects (PTNs) have been produced. A PTN is composed of a nanoparticle head and one or more polymeric tails. Amphiphilic PTNs with asymmetric structures have surfactant behavior and can be used as surfactants in the emulsion or suspension polymerizations.

The nanoparticles used as the heads of the PTNs are manifold. They can be natural proteins or DNAs [7], inorganic nanoparticles [8] or synthetic polymeric nanoparticles [9]. For example, O'Reilly and coworkers used a DNA tetrahedron as the hydrophilic head and a temperature responsive polymer as the tail, and the nanoparticle presents thermal sensitivity [7]. Cheng and coworkers have focused on the synthesis and self-assembly of inorganic nanoparticle-polymer giant surfactants. The giant surfactants can self-assemble into rod micelles, spherical micelles and vesicles, just like the

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small-molecule surfactants in selective solvents [8]. Self-assembled structures with different morphologies were also observed in the self-assembly of giant surfactants composed of an ionic cross-linked polymer head and a hydrophobic polymer tail, as reported in our previous paper [9].

The polymer-tethered single-chain nanoparticles (SCNPs), synthesized by intramolecular cross-linking of block copolymers, have many advantages. For example, it is easy to change the chemical compositions of the structures or perform functionalization on the SCNPs. The functionalized SCNPs can be used to mimic proteins, and will find applications in many fields, including catalysis, sensors and drug delivery. Many different chemical reactions were employed in the synthesis of SCNPs, including reactions of isocyanate functionalized linear copolymers with diamines, cross-linking of the benzosulfone units in polymer chains and olefin cross-metathesis etc [10–13]. The asymmetric SCNPs exhibit interesting properties. For example, the amphiphilic nanoparticles are able to self-assemble into aggregates with different morphologies in selective solvents [9,14]. Herein, we report the synthesis and surfactant behavior of mono-tethered SCNPs with disulfides at the junction points. By using the mono-tethered SCNPs as surfactants, PS colloidal particles with tunable surfaces were prepared.

2. Experimental section

2.1. Materials

2-(Dimethylamino) ethyl methacrylate (DMAEMA) (Across, 99%) was purified by passing through basic alumina column, drying with CaH₂ and distilling under reduced pressure. Styrene (Tianjin Chemical Reagent Company, 98%) was washed with 5% NaOH aqueous solution, dried over anhydrous MgSO₄, and distilled under reduced pressure. ϵ -caprolactone (Alfa Aesar, 99%) was dried with CaH₂ and distilled before use. 2-Hydroxyethyl disulfide (Aldrich, technical grade) and methacryl chloride (TCI, 80%) were distilled before use. CuBr (Alfa Aesar, 98%) was purified by washing with glacial acetic acid and dried in a vacuum oven at 100 °C. 2,2'-Azobisisobutyronitrile (AIBN, Guo Yao Chemical company, AR) was purified by recrystallization from ethanol. Tri-n-butylphosphine (Strem Chemicals, 10% in hexane), 4-(dimethylamino)pyridine (4-DMAP, Alfa Aesar, 99%), 1,4-Diiodobutane (Alfa Aesar, 99%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, Shanghai Medpep Co., Ltd., 99%), tin(II) 2-ethylhexanoate (Sn(Oct)₂, Aldrich, 95%), 2,2'-dipyridyl disulfide (Alfa Aesar, 98%), fluorescein isothiocyanate (FITC, Aldrich, 95%) and *N,N,N,N,N'*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) were used as received. All the solvents were distilled before use.

2.2. Synthesis of 2-bromo-2-methyl-propionic acid 2-(2-hydroxy-ethylthio)ethyl ester

Triethylamine (8.0 mL, 0.050 mol) and 2-hydroxyethyl disulfide (19 mL, 0.10 mol) were dissolved in 30 mL of THF and cooled in ice bath. 2-Bromoisobutyryl bromide (3.0 mL, 0.025 mol) dissolved in 22 mL of THF, was added dropwise into the solution. The solution was stirred in ice bath for 1 h and at room temperature for 24 h. After the reaction, the precipitate was filtered and THF was removed by using a rotary evaporator. The residue was dissolved in dichloromethane and the solution was washed by 3% HCl solution for three times, 2% NaOH solution for three times and water for three times. The organic layer was collected and dried over anhydrous MgSO₄. The crude solution was concentrated by rotary evaporation and purified by column chromatography. Yield: 55%. ¹H NMR, δ (400 MHz, CDCl₃, TMS, ppm): 4.48–4.45 (t, 2H, CH₂–OH), 3.92–3.89 (t, 2H, CH₂–O–C=O), 3.00–2.97 (t, 2H,

HO–CH₂–CH₂–S), 2.92–2.89 (t, 2H, O=C–O–CH₂–CH₂–S), 1.95 (s, 6H, CH₃).

2.3. Synthesis of poly(ϵ -caprolactone) (PCL) using 2-bromo-2-methyl propionic acid 2-(2-hydroxy-ethylthio)ethyl ester as the initiator

Initiator (32 mg 0.11 mmol), ϵ -caprolactone (0.73 mL, 6.6 mmol) and toluene (0.40 mL) were added into a dry Schlenk flask. After one freeze–pump–thaw cycle, Sn(Oct)₂ (5.30 mg, 0.013 mmol) dissolved in 0.30 mL of toluene was added to the Schlenk flask under argon atmosphere. The system was degassed by another freeze–pump–thaw cycle. The polymerization was conducted at 110 °C for 24 h and stopped by exposure to air. The polymer was precipitated in methanol, and dried under vacuum. The apparent number-average molecular weight and the molecular weight distribution of the polymer are 8.0 k and 1.17, respectively.

2.4. Synthesis of poly(ϵ -caprolactone)-s-s-poly(2-(dimethylamino) ethyl methacrylate) (PCL-S-S-PDMAEMA) using PCL-S-S-Br as macroinitiator

The polymerization of DMAEMA was performed by using the PCL-s-s-Br as the macro-initiator. PCL-s-s-Br (0.30 g, 0.034 mmol), DMAEMA (0.460 mL, 2.72 mmol) and 1 mL acetone were added into a Schlenk flask, and in another Schlenk flask CuBr (3.90 mg, 0.0272 mmol), bpy (8.50 mg, 0.0544 mmol) and 0.5 mL acetone were added under argon atmosphere. After one freeze–pump–thaw cycle, the CuBr/bpy solution was transferred into the flask with PCL macro-initiator and monomer, and the solution was degassed by one freeze–pump–thaw cycle. The solution was stirred at 40 °C for 24 h and stopped by exposure to air. The polymer solution was passed through a short alumina column to remove the copper ions. The polymer was purified by precipitating in hexane and dried under vacuum. The apparent number-average molecular weight and the molecular weight distribution of PCL-S-S-PDMAEMA are 13.8 k and 1.25, respectively.

2.5. Intramolecular crosslinking of PCL-S-S-PDMAEMA with 1,4-diiodobutane

A typical procedure for the preparation of SCNPs is described as follows. PCL-S-S-PDMAEMA block copolymer (40 mg) was dissolved in 100 mL of THF. 1,4-Diiodobutane (1.33 μ L) dissolved in 100 mL of THF, was added dropwise into the polymer solution. After one-day reaction, excess triethylamine was added to the mixture and the mixture was concentrated to about 5 mL. The mono-tethered SCNPs were obtained after dialysis of the solution against water and freeze-drying.

2.6. Suspension polymerization of styrene with mono-tethered SCNPs as surfactants

A typical polymerization was described as follows. SCNPs (15 mg) and AIBN (7.2 mg) were dissolved in 0.5 mL of styrene, and the monomer solution was dispersed into 3 mL of water under sonication. The polymerization was performed at 70 °C for 4 h.

2.7. Functionalization of the colloidal particles with pyridyl disulfide

The as-prepared PS colloidal solution was diluted by water and a total 14 mL solution was obtained. PS colloidal particles in 4 mL of the colloidal solution were collected by centrifugation, and the colloidal particles were re-dispersed in acetonitrile. The solution

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