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Synthesis of nylon-6.6 using cetyltrimethylammonium chloride reverse micelles immobilized on silica surfaces

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ABSTRACT

Nylon-6,6 was synthesized in cetyltrimethylammonium chloride reverse micelles adsorbed on silica surfaces to study the feasibility of preparing a surface modified with grafted polyamide brushes using the immobilized reverse micelle as a microreactor. The nylon-modified silica gel preparation procedure involved: (1) adsorption of the CTAC reverse micelles containing 1,6-hexanediamine and sodium hydroxide onto silica gel surfaces, (2) in situ polymerization of 1,6-hexanediamine and adipoyl dichloride at the reversed micellar interfaces, and (3) the removal of residual components such as CTAC or reverse micelles. The nylon produced on silica surface was characterized in detail. The principal interaction in the immobilization of nylon on silica surface may be hydrogen bonding between the terminal amine groups of nylon and the surface silanol groups. Atomic force microscopy images of the nylon monolayers attached to glass plate surfaces showed the formation of grafted polymer brushes or nanoclusters on the surfaces. To characterize the prepared surface of the silica gel, the modified silica gel particles were successfully employed in chromatographic analysis as a stationary phase for the separation of *o*-, *m*-, and *p*-nitroanisoles using cyclohexane as a mobile phase.

1. Introduction

Reverse micelles are generally described as nanometer-sized water droplets or pools dispersed in a non-polar organic solvent with the aid of a surfactant monolayer, forming a thermodynamically stable and optically transparent solution [1]: The water pool in such a micellar core provides a unique and versatile reaction field and can be considered as a nanoreactor. In reverse micelles used as microreactors, many nanosized particles, including metals [2,3], metal sulfides and selenides [4,5], and metal oxides [6,7], have been prepared. Furthermore, reverse micelles should be able to enhance spectrometric techniques by functioning as solubilization media, or intensity amplification agents; there has been thus particular interest in applications of reverse micelles in analytical methods [8].

The adsorption of ionic surfactants on mineral surfaces is a topic of great interest both from industrial as well as academic point of view. The adsorption of surfactants on solid/liquid interfaces is important in several processes, for example, detergency, floatation, wetting behavior, biological phenomenon, pollution control [9,10]. Surfactants distribute to an interface and as a result the interfacial properties are modified significantly. Successful attempts have been made to stabilize normal micelles on solid supports and the process of immobilization has been thoroughly studied in the past [11–13].

Our interest in the immobilization of reverse micelles stems from the utilities of reversed micellar media mentioned above for analytical purposes. In our previous work, the adsorption behavior of reverse micelles of cetyltrimethylammonium chloride (CTAC) onto porous silica gels was examined [14]. Being encouraged from the results, this study was extended to the reverse micelle adsorption onto the silica gels to produce the nanoclusters of polyamide such as nylon-6,6 by interfacial polymerization at the positively charged surfactant-water interface of the micelles immobilized on the silica surfaces. The aims of the present work are to study the feasibility of preparing the surfaces modified with grafted polyamide brushes using the adsorbed reverse micelles as a nanoreactor. Such a grafting-from approach allows for the elaboration of a wide range of polymer brushes with high grafting densities, although a common mismatch between the brushes and the polymer simultaneously grown in the bulk requires a rigorous characterization of the brushes after grafting [15–17]. In the proposed method, the reactant 1,6-hexanediamine in the reverse micelle immobilized on the silica surface is used partly as a surface-immobilized initiator to prepare polymer layers with in situ polymerization. Thus, the produced nylon

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nanostructure may be immobilized on the silica surface through hydrogen bonding between the terminal amine groups of nylon and the surface silanol groups.

The modification with thin polymer layers is widely used in biomedical applications, to provide functionality to surfaces [18]. In this work, we succeeded in synthesizing the nylon-6,6 nanocluster immobilized on the silica surfaces by using the CTAC reverse micelles to form the nanoreactors. In modern science, nanoscience is one of the most important research and development frontiers and the use of nanometer-sized materials or nanoparticles offers many advantages due to their unique size and physical properties [19]. Therefore, the silica surface modified with grafted polyamide brushes or nylon nanoclusters can be expected to bear unique properties of material recognition and separation and to be used as a stationary phase in liquid chromatography. In this work, the silica gel particles modified by the present method was thus used as a stationary phase in chromatographic analysis for the characterization of the silica surface modified with nylon nanoclusters. A study for the separation of positional isomers was carried out successfully, indicating that the stationary phase is stable.

2. Experimental

2.1. Materials

Adipoyl dichloride (>95%), 1,6-hexanediamine (>98%), chloroform (>99.7%, stabilized with amylene), cyclohexane, ethanol (99.5%), and sodium hydroxide were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). The cetyltrimethylammonium chloride (CTAC, 98%) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). *o*-, *m*-, *p*-Nitroanisoles and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Chloroform, cyclohexane, and HFIP were of HPLC grade and all other reagents used were of reagent grade. Silica gel 60 N (with a particle size of 63–210 μm, a pore size of 5.0–7.0 nm, and a BET surface area of 650 ± 50 $m^2\ g^{-1}$) was obtained from Kanto Chemical Co., Inc. The Daisogel® SP-120-10P silica gel (with a average particle size of 9.2 μm, a average pore size of 13.8 nm, and a BET surface area of 293 $m^2\ g^{-1}$), obtained from Daiso, was also used for the transmission electron microscopy (TEM) measurements. All of the chemicals were used as received. Deionized water was freshly collected from an Advantec Toyo (Tokyo) Model GSU-901 water purification apparatus and was utilized in the preparation of all aqueous solutions and related cleaning purpose. All solutions were made fresh before use.

An aqueous solution of 2.77 M 1,6-hexanediamine was prepared in 2.5 M sodium hydroxide. The reversed micellar solution of the diamine used in this work was made in a similar manner as reported previously [20] by dispersing a certain volume (0.36 mL) of the alkaline solution of 1.6-hexanediamine in chloroform (50 mL) containing 0.10 M CTAC. The resultant reversed micellar solution had a water-to-surfactant molar ratio (R = [water] / [CTAC]) of 4 and the 1,6-hexanediamine concentration, calculated on a final volume total solution basis, was 0.020 M. A 0.020 M solution of adipoyl dichloride was prepared in cyclohexane.

2.2. Synthetic procedure

2.2.1. Nylon-6,6 immobilized on porous silica gel

5 g of silica gel was added to 50 mL of the CTAC reversed micellar solution containing 1,6-hexanediamine and sodium hydroxide in a separating funnel, the bottom of which was stoppered prior to each run with glass wool used as a filter. Then the silica gel was suspended in the reversed micellar solution by occasional shaking and the suspension was permitted to stand for about 30 min to get complete adsorption of the CTAC reverse micelle on the silica surface. After the solution had been filtrated off using an aspirator, the silica gel particles in the funnel were rinsed with cyclohexane (30 mL) to take away excess reverse micelles that were not adsorbed. In succession, the silica gel obtained in the funnel after filtrating was mixed with 50 mL of 0.020 M adipoyl dichloride solution and suspended again by frequent shaking for about 30 min, during which time the polymerization of 1.6-hexanediamine and adipoyl dichloride at the surfactant-water pool interface of the reverse micelle immobilized on silica gel was completed. Then, the resulting silica gel particles were filtrated out, rinsed with cyclohexane (30 mL), and then washed consecutively with ethanol (50 mL) and with de-ionized water (50 mL) to remove the residual components such as the adsorbed CTAC and by-product. Finally, the modified silica gel particles were dried at about 65 °C overnight.

2.2.2. Nylon-6.6 immobilized on a glass plate

In a similar manner as above, the preparation of the immobilized nylon, including the polymerization of 1.6-hexanediamine and adipoyl dichloride at the interface of the reverse micelle adsorbed on the glass surface was carried out for the AFM measurements. Before use, a very flat glass plate (1 cm × 1 cm) was immersed in nitric acid for 1 h to clean, thoroughly rinsed with extra-pure water, and dried in an oven. First, the glass plate rinsed was soaked in 50 mL of the CTAC reversed micellar solution containing 1.6-hexanediamine for 30 min to adsorb the reverse micelle on its surface and then rinsed out with 30 mL of cyclohexane. Next, the glass plate obtained was soaked in 50 mL of 0.020 M adipoyl dichloride solution for 30 min to complete the polymerization and then rinsed with 30 mL of cyclohexane. Finally, the resulting glass plate, on the surface of which the produced nylon was immobilized, was soaked in 50 mL of ethanol for 30 min, washed consecutively with 50 mL of de-ionized water and with 10 mL of acetone, and then dried at room temperature.

2.3. Analyses

The adsorption of CTAC and 1,6-hexanediamine onto silica gel in the first step, which was required by the present approach, was investigated. The CTAC and 1,6-hexanediamine molecules adsorbed were retrieved from silica gel using ethanol as an eluent and by serial dilution of the eluent, the sample solutions were made for the following analyses. The amount of CTAC was determined through the quantification of the counter chloride ion of CTAC present in the sample solutions using a Yokogawa (Tokyo, Japan) Model IC-7000 ion chromatographic analyzer. PTFE tubing of 1.0 mm i.d. was used throughout the flow system. A125 mm × 4.9 mm i.d. Yokogawa Excelpack ICS-A44 anion separation column was employed for the ion chromatographic separation at 40°C, which was coupled to a 30 mm × 4.6 mm i.d. Yokogawa Excelpack ICS-A4G guard column. A 50 μL loop was used to load the sample solutions using a syringe manually and then it was inserted in the stream of 4.0 mM Na_2CO_3 and 4.0 mM $NaHCO_3$ carrier driven at the flow rate of 1.0 mL min^{-1}. The eluting chloride ion from the column was monitored by conductometry. The diamine molecules in the sample solutions were also analyzed using a Yokogawa Model G1600A capillary electrophoresis apparatus (Yokogawa Co. Ltd., Tokyo, Japan) with a running voltage of + 20.0 kV. Injections were performed by the action of pressurized air for 4.0 s at 50 mbar. The wavelength used for detection was 310 nm. The length of a Hewlett-Packard (CA, USA) fused-silica capillary of 75 μm i.d. was 560 mm. A solution (pH 3.0) containing 4.0 mM formic acid, 4.0 mM copper(II) sulfate and 3.0 mM 18-crown-6 was used as a buffer. The electrophoretic separation was carried out at 25 °C.

The morphology of silica gel particles coated with nylon was observed using a Hitachi (Tokyo, Japan) Model H-8100 TEM apparatus. For the TEM measurements, the sample was obtained by preparing slices of about 100 nm thickness by using an ultra-microtome, followed by stabilizing the nylon-modified silica gel particles in curing resin. After soaking into the aqueous solution containing stain (phosphotungstic acid) and drying, the cross section of the nylon-coated silica particle was observed at an operating voltage of 200 kV.

Thermogravimetric analysis (TGA) was carried out with a Rigaku Instrument (Tokyo, Japan) Model TG 8120 thermogravimetric analyzer