



# Synthesis and characterization of amphiphilic silica nanoparticles covered by block copolymers branching photochromic diarylethene moieties on side chain



Ryuta Seno, Seiya Kobatake\*

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

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## ABSTRACT

Silica nanoparticles covered with polystyrene branching diarylethene moieties to the side chains are synthesized by reversible addition-fragmentation chain transfer polymerization on silica nanoparticles. The resulting nanoparticles are soluble in toluene and tetrahydrofuran and show reversible photoisomerization upon alternating irradiation with ultraviolet and visible light. The photoreversible isomerization follows color change, which is called photochromism. During the photochromic reactions, the nanoparticles are dispersed in solutions such as tetrahydrofuran. The modification by further block copolymerization of *N*-isopropylacrylamide results in fabrication of photochromic silica nanoparticles soluble in both tetrahydrofuran and water.

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## 1. Introduction

Inorganic nanoparticles covered with organic polymers have drawn much attention as organic/inorganic hybrid materials in recent years because of their applications for optical materials, paints, makeup, column fillers, and solar cells [1–4]. Inorganic silica nanoparticles have characteristics such as simple fabrications of controlled particular size, low cost, weather resistance, chemical resistance, and safeness. Silica nanoparticles covered with the functional dyes are useful as novel functional dyes and pigments which have the potential for toughness and durability. The various types of fluorescent dyes attached on silica nanoparticles have recently been used for reversible fluorescence switch for biological imaging [5–10]. The fluorescence modulation is based on a photochromic molecular switch incorporated into the silica nanoparticles. The biocompatibility of the silica nanoparticles makes promising materials for in vivo imaging applications. Such organic/inorganic hybrid materials can improve the solubility in solvents by the modification of the covering agents.

Photochromic compounds exhibit reversible transformations between two isomers upon irradiation at an appropriate wavelength of light [11,12]. The interconversion between the two states is accompanied by changes in the physical properties such as absorption spectra, fluorescence, refractive indices, dielectric constants, oxidation–reduction potentials, and so on. Diarylethene is one of typical P-type photochromic compounds and shows reversible photoisomerization upon alternating irradiation with ultraviolet (UV) and visible light [13–16]. Silica nanoparticles with diarylethene polymers are expected to be used for application as a photochromic pigment having toughness and durability because of high dispersibility of the particle in organic solvents in addition to thermal stability and fatigue-resistant properties. Photochromic hybrid materials can be applied as photochromic decoloration, photochromic glasses, UV sensors, photochromic optical waveguide, optical memory devices, holographic recording media, non-linear optics, and so on [17].

The “grafting-from” and “grafting-to” techniques in polymer chemistry are commonly used for connecting polymer chains on solid substrate [18–20]. Among them, the former method can connect polymer with functional group on substrate, whereas the latter method can initiate polymerization from substrate on which an initiator or a chain transfer agent presents to form grafting

\* Corresponding author. Tel./fax: +81 6 6605 2797.

E-mail address: [kobatake@chem.eng.osaka-cu.ac.jp](mailto:kobatake@chem.eng.osaka-cu.ac.jp) (S. Kobatake).

polymer chains in high density. Particularly, living radical polymerizations on the surface of materials are widely used for grafting on substrate because of easy control of polymer chain length and end groups. There are some reports on the surface-initiated living radical polymerizations such as atom transfer radical polymerization and reversible addition-fragmentation chain transfer (RAFT) polymerization [21,22]. Tsujii and coworkers found that high-density polymer brushes can be obtained by living radical polymerization from solid substrate [21]. Moreover, they demonstrated that the dispersibility of silica nanoparticles covered with polymer brushes in organic solvents is dominated by the nature of the polymers fabricated onto the silica nanoparticles [23].

Here, we report on fabrication of silica nanoparticles covered with polystyrene having photochromic diarylethene chromophores to the side chains, as shown in Scheme 1. The silica surface-initiated polymerization was carried out by RAFT copolymerization of styrene (St) and a diarylethene monomer (DE) using silica nanoparticle covered with a RAFT agent. To modify the solubility of the nanoparticles in both hydrophobic and hydrophilic solvents, block copolymerization with *N*-isopropylacrylamide (NIPAm) was also performed. The photochromic behavior and dispersibility of the resulting nanoparticles in tetrahydrofuran (THF) and water are discussed.

## 2. Experimental section

### 2.1. Measurements

$^1\text{H}$  NMR spectra were measured using a Bruker AV-300N NMR spectrometer at 300 MHz. Deuterated chloroform ( $\text{CDCl}_3$ ) was used as the solvent and tetramethylsilane (TMS) as internal standard, respectively. Transmission electron microscopy (TEM; Hitachi H-7000) was performed at an accelerating voltage of 75 kV. TEM samples were prepared by dropping an ethanol or THF solution of the particles on a carbon-coated copper grid and dried in air. The particle size was determined from the TEM image. Absorption spectra were measured using a UV/visible absorption spectrophotometer (Jasco V-560). Photoirradiation was conducted using a 200 W mercury–xenon lamp (Moritex MUV-202) or a 300 W xenon lamp (Asahi Spectra MAX-301) as a light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin Yvon H10 UV or Jasco CT-10) and glass

filters. Gel-permeation chromatography (GPC) was performed using a Tosoh 8000 series GPC system equipped with TSK-gel columns at 40 °C and using THF as the eluant.

### 2.2. Materials

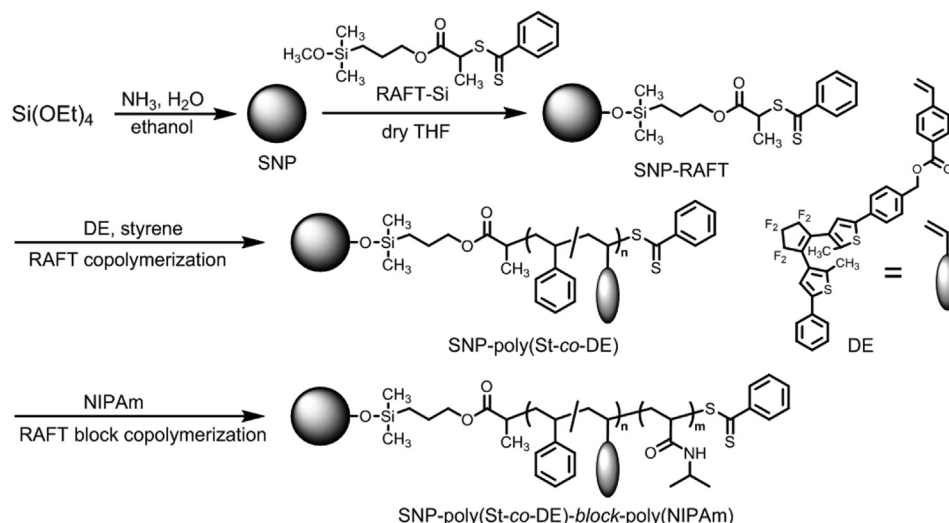
All reagents were purchased from Wako Pure Chemical Industries. NIPAm and 2,2'-azobis(2,4,4-trimethylpentane) (ATMP) were recrystallized from *n*-hexane. DE was synthesized according to the method described in our previous paper [24].

### 2.3. Synthesis of 1-[3-(methoxydimethylsilyl)propyloxycarbonyl]-ethyl dithiobenzoate (RAFT-Si)

RAFT-Si was synthesized according to the method described in literature as follows [25]. Phenylmagnesium bromide was prepared from bromobenzene (12.4 mL, 118 mmol) and magnesium turnings (1.90 g, 78.2 mmol) in dry THF (30 mL). Carbon disulfide (4.80 mL, 79.5 mmol) was slowly added to the THF solution of the Grignard reagent at 40 °C. To the mixture was slowly added 3-(methoxydimethylsilyl)propyl 2-bromopropionate (20.2 g, 71.2 mmol) at 40 °C. The mixture was stirred for 24 h at room temperature. An adequate amount of ice water was added to the mixture to quench the reaction. The reaction mixture was extracted with ether, washed with brine, dried over  $\text{MgSO}_4$ , filtrated, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (8:2) as the eluant. The pure product was obtained by a recycle HPLC (JAI LC-908) on gel columns (JAIGEL-1H and 2H) using  $\text{CHCl}_3$  as the eluant in 72.2% yield (18.3 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  (ppm) = 0.11 (s, 6H,  $\text{Si}(\text{CH}_3)_2\text{OCH}_3$ ), 0.56–0.65 (m, 2H,  $\text{COOCH}_2\text{CH}_2\text{CH}_2$ ), 1.67–1.75 (m, 2H,  $\text{COOCH}_2\text{CH}_2$ ), 1.68 (d,  $J = 7.4$  Hz, 3H,  $\text{SCHCH}_3\text{CO}$ ), 3.41 (s, 3H,  $\text{Si}(\text{CH}_3)_2\text{OCH}_3$ ), 4.09–4.17 (m, 2H,  $\text{COOCH}_2$ ), 4.75 (q,  $J = 7.4$  Hz, 1H,  $\text{SCHCH}_3\text{CO}$ ), 7.26–7.57 (m, 3H, Aromatic H), 7.97–8.01 (m, 2H, Aromatic H).

### 2.4. Synthesis of 1-(ethoxycarbonyl)ethyl dithiobenzoate (EEDB)

EEDB was synthesized according to the method described in literature as follows [26]. Phenylmagnesium bromide was prepared from bromobenzene (10.5 mL, 100 mmol) in THF (50 mL) and magnesium turnings (2.43 g, 100 mmol) in dry THF (7 mL) by heating for 20 min at 60 °C. Carbon disulfide (6.10 mL, 101 mmol)



**Scheme 1.** Synthetic scheme of an amphiphilic photochromic silica nanoparticle.

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