

## TEMPO Radical Polymer Grafted Silicas as Solid Oxidation Catalysts

Kei Saito<sup>b</sup>, Koji Hirose<sup>a</sup>, Teruyuki Okayasu<sup>a</sup>, Milton T. W. Hearn<sup>\*b</sup>, and Hiroyuki Nishide<sup>\*a</sup>

<sup>a</sup>*Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan*

<sup>b</sup>*Centre for Green Chemistry, Monash University, Clayton, Victoria 3800, Australia*

### Supporting Information

*N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ), fumed silica, and mono-TEMPO Si were purchased from Sigma-Aldrich (2-2-24, Higashishinagawa, Shinagawa-ku, Tokyo, Japan). Other chemicals were purchased from Tokyo Chemical Industry Co. Ltd. (4-10-2 Nihonbashi, Tokyo, Japan). <sup>1</sup>H NMR spectra were recorded using a JEOL-Lambda 500 and ECX 500 spectrometers. The organic content of the synthesized materials was quantified by elemental analysis performed on a Carlo Erba Elemental Analyser EA CHNS analyzer. Fourier transform infrared (FT-IR) spectra of samples were recorded on JASCO FT/IR-6100 with KBr pellet technique. SEM images were recorded on a Hitachi S4500S field-emission scanning electron microscope. The magnetic susceptibility was measured from 1.95 to 270 K in a 0.5 T field for radical concentration estimation using Quantum Design MPMS-7 SQUID magnetometer. Mass spectra were recorded using JMS-SX102A / Shimadzu GCMS-QP5050 spectrometer.

#### 1. Synthesis of S-methoxycarbonylphenylmethyl S'-trimethoxysilylpropyltrithio-carbonate

The synthesis of S-methoxycarbonylphenylmethyl S'-trimethoxysilylpropyltrithio-carbonate was adapted from the method described by Zhao and Perrier (Y. Zhao, S. Perrier, *Macromolecules* **2007**, *40*, 9116-9124). The product was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI-MS: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.31 (m, 5H, PhH), 5.81 (s, 1H, CH), 3.74 (s, 3H, CH<sub>3</sub>), 3.55 (s, 9H, CH<sub>3</sub>O), 3.37 (t, *J*<sub>7</sub>, 2H, CH<sub>2</sub>S), 1.82 (m, 2H, CH<sub>2</sub>), 0.75 (t, *J*<sub>8</sub>, 2H, CH<sub>2</sub>Si). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 221.9, 169.5, 133.2, 129.1, 128.8, 128.7, 58.0, 53.3, 50.4, 39.8, 21.9, 8.9. IR (cm<sup>-1</sup>):

1742( $\nu_{C=O}$ ), 1601( $\nu_{Ph}$ ), 1495( $\nu_{Ph}$ ), 1083( $\nu_{SiO}$ ), 1050( $\nu_{C=S}$ ), MS(m/z): 419.0 (found), 420.6 (calcd).

## 2. Synthesis of (4-cyano-4-[(phenylthioxomethyl)thio]-1-(2-carboxyethyl)-1-cyanoethyl benzodithioate)

The synthesis of (4-cyano-4-[(phenylthioxomethyl)thio]-1-(2-carboxyethyl)-1-cyanoethyl benzodithioate) was adapted from the method described By Oliveira et al. (M. A. M. Oliveira, C. Boyer, M. Nele, J. C. Pinto, P. B. Zetterlund, T. P. Davis, *Macromolecules* **2011**, *44*, 7167-7175). The product was characterized by  $^1H$  NMR,  $^{13}C$  NMR and ESI-MS:  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.90 (t, 2H, PhH), 7.57 (t, 1H, PhH), 7.40 (t, 2H, PhH), 2.63 (t, 2H,  $CH_2$ ), 2.45 (t, 2H,  $CH_2$ ), 1.95 (s, 3H,  $CH_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  169.8, 144.4, 133.1, 128.6, 126.7, 122.4, 41.1, 33.0, 29.4, 24.2. IR ( $cm^{-1}$ ): 2500-3500 ( $\nu_{COOH}$ ), 1712 ( $\nu_{C=O}$ ), 1048 ( $\nu_{C=S}$ ), MS (m/z): 280.1 (found), 279.4 (calcd).

## 3. Synthesis of TEMPO polymer grafted silica 2 by RAFT polymerization

Synthesis of the TEMPO polymer grafted silica **2** by the “grafting from” method: Fumed silica (1.0 g) was mixed with 30 mL of anhydrous toluene and sonicated for 15 min. S-methoxycarbonyl-phenylmethyl S'-trimethoxysilylpropyltrithiocarbonate (8.41 g, 20 mmol) was then added to the mixture under nitrogen, which was stirred at 100°C for 16 hr and 120°C for 3 hr. After this time, the reaction mixture was centrifuged (4000 rpm for 10 min x 5 times) and freeze dried to yield **1** (0.9 g) as a yellowish powder. 2,2,6,6-Tetra-methylpiperidine methacrylate (5.41 g, 24 mmol) and S-methoxy-carbonylphenylmethylS'-trimethoxysilylpropyl-trithiocarbonate (33.7 mg, 0.08mmol) were dissolved in anhydrous toluene (8 mL) and mixed with **1** (142 mg, 0.08 mmol). After sonication for 10 min, 2,2-azobisisobutyronitrile (2.62 mg, 0.016 mmol) was then added and the reaction mixture stirred for 20 hr at 70°C under nitrogen. After centrifugation (4000 rpm for 10 min x 5 times) and freeze drying, the precursor compound, poly(2,2,6,6-tetramethylpiperidine methacrylate) grafted silica (152 mg) was obtained as a yellowish powder from the reaction solution. The poly(2,2,6,6-tetramethylpiperidine meth-acrylate) grafted silica (152 mg) was treated with 3-chloroperoxy-benzoic acid

(350 mg, 2 mmol) in anhydrous THF (10 mL) for 3 hr at room temperature to yield **2** (151 mg) as a reddish powder. IR( $\text{cm}^{-1}$ ): 2969 ( $\nu_{\text{alkyl}}$ ), 1724 ( $\nu_{\text{C=O}}$ ), 1104 ( $\nu_{\text{SiO}}$ ).

#### 4. Aminolysis reaction to remove grafted polymer from **2**

A solution of sodium hydrosulfite (0.1 M) was added drop-wise to poly(2,2,6,6-tetramethylpiperidine methacrylate) grafted silica (50 mg) in anhydrous THF (3 mL) followed by the addition of 1-hexylamine (0.1 mL, 1 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 16 hr. The solution was centrifuged (4000 rpm for 10 min x 3 times) and added to hexane to precipitate the product as a amorphous polymer.

#### 5. Typical synthesis of poly(PTMA) **3**

2,2,6,6-Tetramethylpiperidine methacrylate (2.25 g, 10 mmol), (4-cyano-4-[(phenyl-thiooxomethyl)-thio]-1-(2-carboxyethyl)-1-cyanoethyl benzodithioate) (28 mg, 0.1 mmol), 2,2-azobisisobutyronitrile (1.60 mg, 0.01 mmol) were dissolved in anhydrous toluene (5 mL) and stirred for 20 hr at 70°C under nitrogen. After this time, the reaction mixture was poured into hexane to precipitate the product. The polymer was obtained as an off-white powder (1.64 g, yield: 73%). This precursor polymer (1.13 g, 5 mmol) was treated with 3-chloroperoxybenzoic acid (2.59 g, 15 mmol) in anhydrous THF (100 mL) for 3 hr at room temperature to yield **3** (1.61 g, yield: 98%) as a reddish powder. The product was characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.18-7.36 (br, 5H, PhH), 5.07 (br, 1H, CH), 1.71-1.93 (br, 4H,  $\text{CH}_2$ ), 1.23 (s, 3H,  $\text{CH}_3$ ), 0.88-1.02 (br, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 164.3, 132.3, 128.9, 126.5, 125.1, 51.4, 47.5, 34.9, 29.0, 23.1, 17.6.

#### 6. Synthesis of amino functionalized silica

Fumed silica (1.0 g) was reacted with (3-aminopropyl)trimethoxysilane (3.56 g, 20 mmol) in anhydrous toluene (80 mL) for 16 hr at 85°C under nitrogen to yield the amino-functionalized silica (1.15 g). IR ( $\text{cm}^{-1}$ ): 2928 ( $\nu_{\text{C-C}}$ ), 558 ( $\nu_{\text{NH}}$ ), 95 ( $\nu_{\text{SiO}}$ ), Elemental anal.; C: 9.26%, H: 2.01%, N: 2.96%.

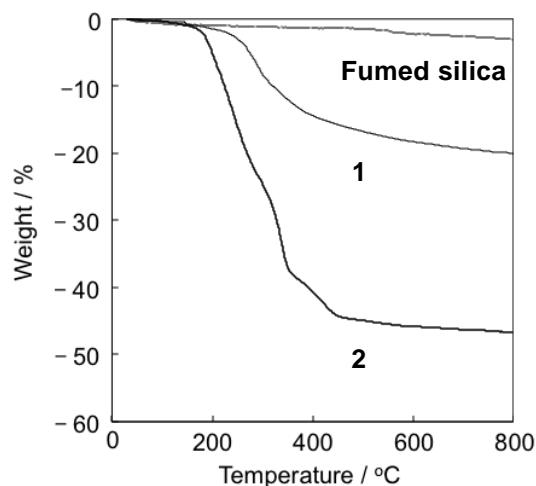
TEMPO polymer grafted silica **4** synthesis by “grafting to” method: The amino-functionalized silica (400 mg) was suspended in anhydrous toluene (10 mL) and sonicated for 15 min. Poly(PTMA) (1.12g, 0.04 mmol) and EEDQ (0.2 g, 0.8 mmol) were dissolved in anhydrous toluene (30 mL) and added slowly to the amino-functionalized silica suspension. The reaction was stirred for 3 days under nitrogen at room temperature. After this time, the reaction mixture was centrifuged, and the product vacuumed dried to yield **4** (573 mg) as a reddish powder. IR ( $\text{cm}^{-1}$ ): 2976 ( $\nu_{\text{alkyl}}$ ), 1726 ( $\nu_{\text{C=O}}$ ), 1648 ( $\nu_{\text{Ph}}$ ), 1540 ( $\nu_{\text{Ph}}$ ), 1099 ( $\nu_{\text{SiO}}$ ), Elemental anal.; C: 34.6%, H: 5.23%, N: 3.94%.

### **7. Typical conditions for the oxidation of alcohols**

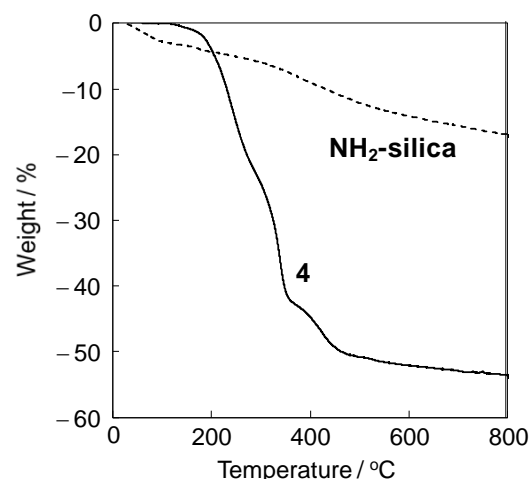
The alcohol (4 mmol) was mixed with the catalyst (0.02 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$  at  $5^\circ\text{C}$ . A solution of KBr (0.5 M, 0.8 mL) and NaOCl (0.35 M, 14.3 mL with the pH adjusted to pH 9 by  $\text{NaHCO}_3$ ) was added to the reaction mixture, which was then stirred for 10 min at  $5^\circ\text{C}$ . After this time, the catalyst was removed by filtration, the organic layer recovered and the  $\text{CH}_2\text{Cl}_2$  removed by gentle rotary evaporation to yield the product. The products were characterised by the methods described in the section entitled Supplementary Material. Analogous procedures were employed with water and the other solvent systems.

## 8. Thermogravimetric analysis

TGA curves of the samples were measured using a Rigaku TG8120 over the temperature range from 30 to 800°C at the heating rate of 10°C min<sup>-1</sup> under an N<sub>2</sub> atmosphere.



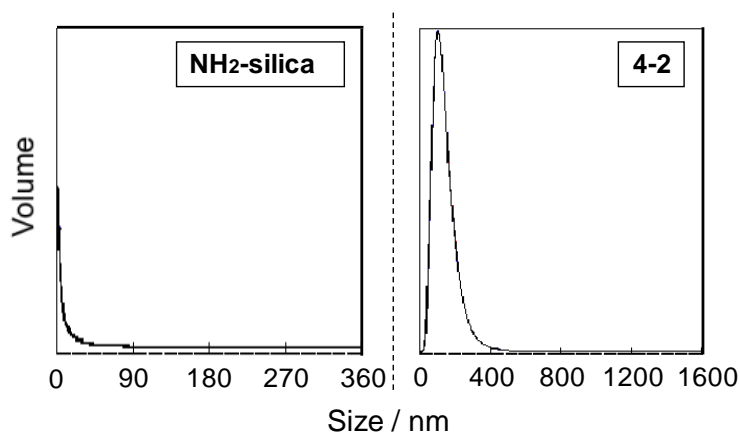
**Figure S2.** TGA curve of fumed silica, **1** and **2** at the heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>.



**Figure S3.** TGA curve of amino functionalized silica and **4-2** at the heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>.

## 9. Dynamic Light scattering

DLS was determined by DAWN EOS 18 Angles Laser Light Scattering Instrument (Wyatt Technology).



**Figure S4.** Size distribution of amino functionalized silica and **4-2**.