



Preparation and properties of silicate particles covalently bonded with phenolphthalein



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ABSTRACT

A silicate particle covalently bonded with phenolphthalein was prepared by a sol–gel method. This particle contained *ca.* 10% of organic component, turned pale pink at pH 10.9, and showed good coloration–discoloration repetition stability.

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1. Introduction

There are two methodologies to obtain pH sensors in dye chemistry: fluorogenic and chromogenic changes. The use of fluorescence-dye-containing silica nanoparticles have been reported in connection with intracellular pH micro-circumstance imaging [1–3]. Meanwhile, the color change of halochromic dyes is more practical to recognize the pH value in more conventional application. From the viewpoint of the structure, there are two kinds of organic/inorganic hybrid materials: organic dyes physically doped in the host inorganic materials and organic dyes covalently bonded with inorganic material. Silica gel doped with azo dyes [4–6], triarylmethane dyes [7,8], and an alizarin derivative [9] have been reported. The important advantages of covalently bonded silicate is its high stability. Though many kinds of organic/inorganic materials have been reported [10–13], to our knowledge, no silicates covalently bonded with well-known phenolphthalein have been prepared so far. We report here its synthesis and properties.

2. Experimental

2.1. Instruments

Melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus. NMR spectra were taken with a JEOL JNM-ECX 400P spectrometer. Mass spectra were taken on a JEOL MStation 700 spectrometer. IR spectra were obtained by a Shimadzu Affinity-1 spectrophotometer. Elemental analysis was performed with a Yanaco MT-6 CHN corder. Reflection spectra were taken on a Hitachi U-3500 spectrophotometer. TG/DTA was performed with a Shimadzu DTG-50 instrument. A polarization microscope Olympus BX53F was used.

2.2. Materials

Phenol (**1**), tin(II) chloride dihydrates, 3-triethoxysilylpropyl isocyanate (**5**), and tetraethoxysilane (TEOS) were purchase from TCI Co., Ltd., Kanto Chemical Co., Inc., Wako Pure Chemical Industries, Ltd., and Nakalai Tesque Inc., respectively. 4-

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Nitrophthalic anhydride (**2**) was synthesized as described in literature [14].

2.3. Synthesis of **3**

To phenol (1, 470 mg, 5.0 mmol) were added 4-nitrophthalic anhydride (**2**, 480 mg, 2.5 mmol) and methanesulfonic acid (5.5 mL). The mixture was heated at 90 °C overnight. After the reaction was completed, the mixture was cooled to room temperature and poured into ice-water with stirring. The resulting precipitate was filtered. Then, the precipitate was dissolved in ethyl acetate (10 mL). To the solution was added charcoal (200 mg), heated, and filtered. The filtrate was concentrated *in vacuo*. The resulting precipitate was recrystallized from ethyl acetate-chloroform (1:20) mixed solvent. Yield 28% (256 mg); mp 239–247 °C; ¹H NMR (DMSO-*d*₆) δ = 6.75 (d, *J* = 8.7 Hz, 4.0 H, H^a and H^{a'}), 7.09 (d, *J* = 8.7 Hz, 2.4 H, H^b), 7.12 (d, *J* = 8.7 Hz, 1.6 H, H^b), 8.03 (d, *J* = 8.2 Hz, 0.6 H, H^c), 8.17 (d, *J* = 8.2 Hz, 0.4 H, H^c), 8.43 (d, *J* = 8.2 Hz, 0.4 H, H^d), 8.44 (s, 0.4H, H^c), 8.57 (s, 0.6 H, H^c), 8.59 (d, *J* = 8.2 Hz, 0.6 H, H^d), 9.72 (s, 0.8 H, O H), 9.74 (s, 1.2H, OH⁺); IR (KBr) $\tilde{\nu}$ 3366, 1751, 1539; EIMS (70 eV) *m/z* (rel intensity) 363 (M⁺, 43), 319 (13), 302 (37), 273 (100); HRMS (EI) *m/z* calcd for C₂₀H₁₃NO₆ (M⁺) 363.0743, found 363.0742.

2.4. Synthesis of **4**

To an ethanol solution (2.5 mL) of **3** (430 mg, 1.2 mmol) was added tin(II) chloride dihydrates (1.36 g, 6.0 mmol). The mixture was heated at 70 °C for 40 min. After the reaction was completed, the mixture was cooled to room temperature and poured into ice-water (60 mL). The product was extracted with ethyl acetate (100 mL) and dried over anhydrous magnesium sulfate. To the solution was added charcoal (2 g), heated filtered, and concentrated *in vacuo* to give pale brown precipitate. Yield 338 mg (85%); mp 138–142 °C; ¹H NMR (DMSO-*d*₆) δ = 6.29 (br s, 2.0H, NH₂), 6.55 (s, 0.4H, H^c), 6.68 (d, *J* = 8.2 Hz, 0.4H, H^d), 6.71–6.75 (m, 4.0 Hz, H^a and H^{a'}), 6.89 (s, 0.6H, H^c), 6.97 (d, *J* = 8.2 Hz, 0.6 H, H^d), 7.01–7.04 (m, 4.0 H, H^b and H^{b'}), 7.32 (d, *J* = 8.2 Hz, 0.6 H, H^e), 7.47 (d, *J* = 8.2 Hz, 0.4 H, H^e), 9.56 (s, 1.2 H, OH⁺), 9.59 (s, 0.8 H, OH); IR (KBr) $\tilde{\nu}$ 3372, 3244, 1728, 1601; EIMS (70 eV) *m/z* (rel intensity) 333 (M⁺, 79), 289 (100), 240 (51), 212 (23); HRMS (EI) *m/z* calcd for C₂₀H₁₅NO₄ 333.1001 (M⁺), found 333.1010.

2.5. Synthesis of **6**

To ethyl acetate (10 mL) were added **4** (200 mg, 0.6 mmol) and 3-triethoxysilylpropylisocyanate (**5**, 148 mg, 0.6 mmol). The mixture was refluxed for 48 h. After the reaction was completed, the mixture was concentrated *in vacuo*. To the resulting precipitate, ethyl acetate (5 mL) was added to dissolve the product. The solution was poured into chloroform to provide the precipitate, which was filtered and dried *in vacuo* to afford yellow solid. Yield 70 mg (20%); mp > 300 °C; ¹H NMR (DMSO-*d*₆) δ = 0.54–0.60 (m, 2.0 H, Hⁱ and H^j), 1.13–1.20 (m, 9.0 H, Hⁱ and H^j), 1.47–1.53 (m, 2.0 H, Hⁱ and H^j), 3.08–3.10 (m, 2.0 H, H^h and H^{h'}), 3.70–3.78 (m, 6.0 H, H^k and H^{k'}), 6.31–6.34 (m, 0.6 H, NH^g), 6.39–6.42 (m, 0.4 H, NH^g), 6.74–6.78 (m, 4.0 H, H^a and H^{a'}), 7.03–7.08 (m, 4.0 H, H^b and H^{b'}), 7.43 (d, *J* = 8.2 Hz, 0.4 H, H^d), 7.57 (d, *J* = 8.2 Hz, 0.6 H, H^e), 7.62 (d, *J* = 8.2 Hz, 0.6 H, H^d), 7.73 (d, *J* = 8.2 Hz, 0.4 H, H^e), 7.83 (s, 0.4 H, H^c), 8.04 (s, 0.6 H, H^c), 8.87 (s, 0.6 H, NH^f), 9.12 (s, 0.4 H, NH^f), 9.63 (s, 1.2 H, OH⁺), 9.66 (s, 0.8 H, OH); IR (KBr) $\tilde{\nu}$ 3337, 2974, 2936, 1740; FABMS (NBA) *m/z* 581 (MH⁺); HRMS (FAB, NBA) *m/z* calcd for C₃₀H₃₇N₂O₈Si: 581.7083 (MH⁺), found 581.7063.

2.6. Synthesis of **7**

To an ethanol solution (0.5 mL) of **6** (0.1 mmol) was added tetraethoxysilane (TEOS, 187 mg, 0.9 mmol) and stirred for 40 min at room temperature. Then, to the solution was added an ethanol solution (0.5 mL) of hydrochloric acid (1.2 mol%). The molar ratio among **6**: TEOS: hydrochloric acid: water was 1.0: 9.0: 0.12: 24. The resulting precipitate was washed with DMSO (2 times), 0.1 M sodium hydrogen carbonate (2 times), 0.1 M acetic acid (2 times), water (2 times), and ethanol (2 times), and dried *in vacuo* to give pale yellow solid (20 mg).

The elemental analysis of **7** indicated that carbon and nitrogen contents were 30.17 and 3.05%, respectively.

On the basis of the carbon content, the *m* and *n* values in Scheme 1 were calculated. The carbon content corresponds to (the number of carbon atoms × 12 × *n*)/(whole molecular weight of **7**). Therefore, equations (1) and (2) are derived:

$$0.3017 = 24 \times 12 \times n / (60m + 417n) \quad (1)$$

$$m + n = 1.00 \quad (2)$$

where *m* and *n* represent the ratio of inorganic silicate and phenolphthalein-containing organic moieties in **7**, respectively. From the equations (1) and (2), *m* and *n* are calculated to be 0.90 and 0.10, respectively.

On the basis of the nitrogen content, the *m* and *n* values were also calculated by the following equation. The nitrogen content corresponds to (the number of nitrogen atoms × 14 × *n*)/(whole molecular weight of **7**).

$$m + n = 1.00 \quad (3)$$

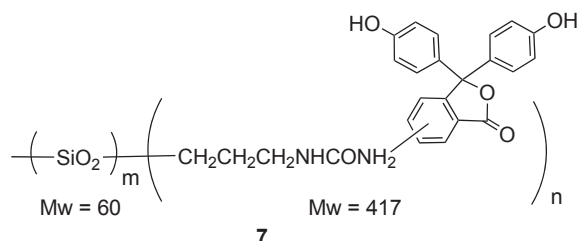
$$0.0305 = 2 \times 14 \times n / (60m + 417n) \quad (4)$$

m and *n* values were calculated to be 0.89 and 0.11, respectively.

Thus, similar results were obtained from the carbon and nitrogen contents. Therefore, the *m* and *n* values were estimated to be 0.9 and 0.1, respectively.

2.7. Repetition test

To dried **7**, a drop of pH 10.9 buffer solution was added and dried. Then, the reflection spectrum of colored **7** was measured. Then, the colored **7** was washed with aqueous 1 M acetic acid (1 mL), water (2 mL), and ethanol (2 mL). This process was repeated two times upon sonication (38 kHz, 5.0 min). The compound **7** was dried *in vacuo* and the reflection spectrum of discolored **7** was measured. This coloration and discoloration process was repeated.



Scheme 1. Calculation of organic content in **7**.

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