Versatile and Facile Preparation of Chiral Polyacetylene-Based Gel Film and Organic−Inorganic Composites

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A new SiH-containing chiral polyacetylene, poly[*p*-[{(*S*)-2-methylbutyl}methylsilyl]-phenylacetylene] (**1**), with a moderate molecular weight (M_w 4.4 × 10^4; M_w/M_n 2.4) was obtained with $[RhCl(nbd)]_2-NEt_3$ catalyst. IR and ^1H NMR studies revealed that the SiH group in **1** remains intact, with no side reactions such as hydrosilylation and hydrolysis. Furthermore, **1** readily turned into a transparent gel film with Si−O−Si linkages simply by standing in air at room temperature. The polymer **1** exhibited a quite large optical rotation ($[\alpha]_D = 600°$, $c = 0.12$ g/dL in toluene at 25 °C), corresponding to large molar ellipticities ($[\theta]_{ext} = -5.1 \times 10^3$ deg·cm^2·dmol^{-1} at 326 nm and 4.7×10^3 deg·cm^2·dmol^{-1} at 371 nm). The CD intensity of the gel film scarcely changed in the range from 25 to 85 °C, presumably due to Si−O−Si cross-linking. Moreover, organic−inorganic composite materials were easily obtained by stirring inorganic particles such as titania and silica gel in the polymer solution. The prepared composites were characterized by AFM, EDX, and SEM.

Introduction

Chiral polymers play crucial roles as HPLC chiral stationary phase and optical resolution membrane in the fields of medicine and agricultural chemicals, in which optically pure forms are required for the safety of the human body.[1] Some chiral polyacetylenes may be promising materials for optical resolution, due to their excellent membrane-forming ability and high permselectivity to chiral racemic compounds.[1c,2] However, both in adsorption and permeation performances, mobile phase solvents were restricted to water, alcohols, and hexane because these polyacetylenes readily dissolve in organic solvents such as benzene, toluene, chloroform, THF, cycloalkanes, and so on. Recently, Masuda and Teraguchi have developed a completely insoluble and well-defined chiral poly(diphenylacetylene) membrane by a unique desilylation reaction method.[3] This kind of insoluble chiral polymeric material may be useful for enantioseparation, which permits us to use various organic solvents as the mobile phases.[3a] Despite this advantage, little attention has been paid to a chiral polyacetylene-based gel because of the handling difficulty ascribed to the intrinsic insolubility.

Most chiral polyacetylenes are obtained from monosubstituted acetylenes because the cis−transoidal structure of the main chain can be easily obtained by using Rh and Fe catalysts, which is favorable for the induction of one-handed screw-sense conformation.[4] However, there are some problems such as chemical and thermal instability in their practical uses. For example, cis−transoidal poly(phenylacetylene)s prepared with Rh catalyst readily undergo autoxidative degradation into oligomers[5] and their helical conformations are thermally unstable.[6] Although conventional cross-linked polymers always give little spectroscopic information about their purities and conformational structures because of the insolubility, polymer gels are promising for chemically and thermally stable materials. Sol−gel reaction of

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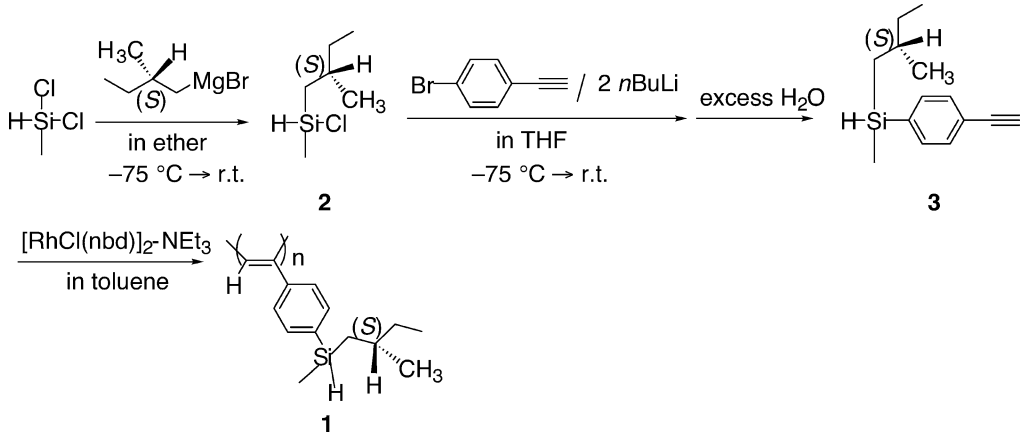
Scheme 1. Synthesis of Poly[*p*-[{(*S*)-2-methylbutyl}methylsilyl]phenylacetylene], 1



alkoxysilane in various organic polymer matrixes often provides transparent, homogeneous gel films which show enhanced chemical and thermal stability due to the siloxane (Si−O−Si) cross-linkages.[7] Thus, we are now interested in developing a more facile synthetic method and clean process of such gel films based on chiral polyacetylenes preferably without evolution of any volatiles.

In addition, chemical surface modification of silica, mica, and metal oxides via covalent bonding of organosilicon derivatives such as chlorosilanes (SiCl), alkoxysilanes (SiOR), and hydrosilanes (SiH) is very useful for various applications including HPLC stationary phase, adhesion, sensor, and optical/electronic devices.[8] In the formation of Si−O linkages between the organosilicon derivatives and the inorganic particles (substrates), chloro- and alkoxysilanes necessarily liberate HCl gas and alcohols, respectively, as byproducts which might lead to a reduced reaction rate and substrate corrosion, while hydrosilanes evolve harmless hydrogen gas or water.[9] Furthermore, SiH group tolerates many reactions compared to SiCl and SiOR groups. Thus, it is interesting to synthesize SiH-containing polymer which possesses potential as a surface-modifying agent for preparing polymer−inorganic composites.

In this work, we synthesized a novel SiH-containing chiral poly(phenylacetylene) with no structural defects. The resulting polymer easily turned into a transparent gel film with Si−O−Si cross-linkages simply by standing in air, and the CD intensity of the gel film hardly changed in the range from 25 to 85 °C. Furthermore, surface coating of inorganic particles such as titania and silica gel with the polymer was successfully achieved.

Results and Discussion

As mentioned above, gelation (cross-linking) and chemical surface modification techniques are the key points in improving the durability of stationary phases against many organic solvents.[10] To prepare a gel film and organic−inorganic composites based on chiral polyacetylene, we designed a new SiH-containing polymer, poly[*p*-[{(*S*)-2-methylbutyl}methylsilyl]phenylacetylene] (**1**), as shown in Scheme 1. Lithiation of *p*-bromophenylacetylene with 2 equiv of *n*-butyllithium followed by reaction with 1 equiv of [(*S*)-2-methylbutyl]methylchlorosilane (**2**) yielded the target monomer, *p*-[{(*S*)-2-methylbutyl}methylsilyl]phenylacetylene (**3**), as a clear, colorless liquid in 43% yield. Hydrosilanes readily hydrolyze in the presence of some transition metal catalysts such as Pd, Pt, and Rh.[11] To prevent the hydrolysis, the polymerization of **3** with $[RhCl(nbd)]_2$−NEt_3 was conducted in dry toluene at room temperature under dry nitrogen gas, which quantitatively provided **1** with a moderate molecular weight (M_w 44 × 10^3; M_w/M_n 2.4). The polymer **1** spontaneously turned to a gel in the course of purification as follows: precipitation to wet methanol, vacuum-drying, and then standing in air for several hours. The gel formed was completely insoluble in a wide range of organic solvents such as toluene, chloroform, tetrahydrofuran, and so on, while the polymerization system was completely clear and soluble. Presumably, SiH groups were converted to SiOH by aerial oxidation and/or hydrolysis, and then the dehydrocoupling of SiH/SiOH in methanol formed the inter- and intramolecular Si−O−Si linkages. Thus, to maintain solubility, the polymer was immediately dissolved in dry toluene (stock solution, $c = 12$ mg/mL) after precipitation in dry methanol and subsequent drying in a nitrogen gas atmosphere and in a vacuum and then stored in a refrigerator.

Figure 1 shows a well-defined structure of the present polymer, **1**: (1) The IR spectrum exhibited no absorption at 3300 cm^{-1} due to the ethynyl group, while the SiH absorption peak at 2170 cm^{-1} remained as it was in **3**. (2) The ^1H NMR spectrum clearly showed a SiH proton peak at 4.31 ppm (c) and a characteristic *cis*-alkenylenic proton peak at 5.82 ppm (e). (3) The peak ratio of the aromatic (d), alkenylenic (e), SiH (c), and methyl (a) group resonances is about 3.9:1.0:0.9:3.0, which agrees

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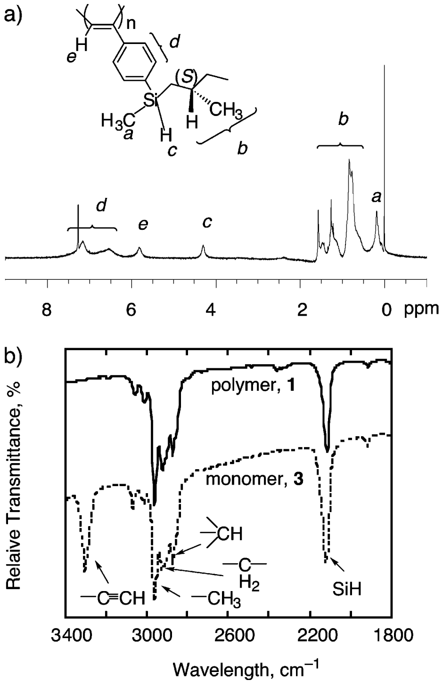

Figure 1. (a) ^{1}H NMR (in $CDCl_3$) and (b) IR (cast film on KBr) spectra of **1**.

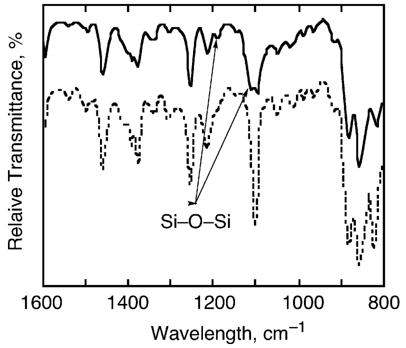

Figure 2. IR spectra of polymer gel film (—) and monomer (- - -).

well with the theoretical ratio (4:1:1:3). (4) From the peak ratio of alkenylenic and aromatic protons, the cis content of the present polymer is calculated to be >99%. These spectral data indicate that the Rh catalyst selectively catalyzes polymerization of **3** via an insertion mechanism rather than hydrosilylation and produces the stereoregular polyacetylene with almost 100% cis structure.

The polymer **1** turned to a transparent, insoluble gel film simply by standing in air at room temperature for several minutes after casting the toluene solution. As shown in Figure 2, the IR spectrum of the gel film exhibited two characteristic absorptions at 1180 and 1110 cm^{-1} due to the Si−O−Si linkage, which were not observed for **3**. Moreover, the intense SiH absorption peak still remained after gelation as shown in Figure 1b. This indicates that only a small fraction of SiH groups take part in gelation under such conditions, and most of the SiH groups remain intact. Figure 3 shows the proposed schematic gelation reaction. Thus, it could be expected for the gel film to be used not only for further gelation at a higher temperature than room temperature but also for further functionalization reactions such as hydrosilylation in a swollen state. The gel film swelled in organic solvents such as chloroform, benzene, toluene, and *o*-dichlorobenzene, while it appeared to slightly shrink in alcohols.

The UV−visible spectrum of **1** in toluene showed two characteristic absorption maxima at $\lambda_{max} = 330$ nm ($\epsilon_{max} = 9600$ M^{-1} cm^{-1}) and 409 nm ($\epsilon_{max} = 6200$ M^{-1} cm^{-1}) due to the $\pi-\pi^*$ transition of the backbone, and virtually no absorption above 500 nm. This polymer showed a very large optical rotation ($[\alpha]_D = 600°$, $c = 0.12$ g/dL in toluene, at room temperature). The CD spectrum of the polymer exhibited quite large molar ellipticities $[\theta]$ in the backbone absorption region in toluene at 25 °C: $[\theta]_{ext} = -5.1 \times 10^3$ deg·cm^2·dmol^{-1} at 326 nm and 4.7×10^3 deg·cm^2·dmol^{-1} at 371 nm. Figure 4 shows the temperature dependence of the CD spectra of the polymer in solution and gel−solid states. Similar to conventional helical polyacetylenes, the magnitude of the Cotton effect gradually decreased in solution state as the temperature increases from 25 to 85 °C. This result indicates that the helical conformation of the present polymer is not sufficiently stable in solution state even at room temperature. In contrast, the CD intensity of the gel film hardly changed in the same temperature range. Presumably, the helical conformation is tightly locked by Si−O−Si cross-linking.

To demonstrate a possibility that the present SiH-containing chiral polymer can be used as a coating material which covalently bonds to the hydrated surfaces of titania and silica gel, we cast the dilute polymer solution ($c = 4.4 \times 10^{-6}$ M, in toluene) on mica and washed with toluene several times before imaging the microstructure of the polymer using an atomic force microscope (AFM). Figure 5a shows the AFM image of the polymer. Globule-like molecular images were uniformly seen on the surface of mica, indicating a production of nanosized aggregates. Fadeev and co-workers reported that although the reaction mechanism is unknown, transition metal oxides such as titania work like Lewis acid, and so effectively catalyze the oxidation and/or hydrolysis of hydrosilanes, leading to formation of Si−O bonds on the surfaces.[9a] This implies that the present polymer may form covalent Si−O bonds on the hydrated surfaces of titania, silica gel, and mica. In fact, the present SiH-containing polymer was likely to react with the inorganic particles. As shown in Figure 5b, both titania (Aldrich, rutile, <5 μm) and silica gel (Merck, silica gel 60, 60−200 μm) became pale yellow, which is the color of the polymer, after stirring in the polymer solution ($c = 12$ mg/mL in toluene) for a few hours at room temperature and washing with toluene several times.

Figure 5c shows the scanning electron microscope (SEM) image of the titania coated with **1**. The average size of the particles was mostly less than 5 μm, which changed little compared to that of bare titania. As shown in Figure 5d, however, the energy-dispersive X-ray spectroscopy (EDX) revealed that the sample consists of titanium, oxygen, carbon, and silicon. The carbon content was determined to be between 15 and 20 wt %, depending on the region of the sample. Also, a highly uniform distribution of carbon was readily seen from an X-ray elemental map. It is thus confirmed that the nanosized polymer chains uniformly attached to the surface of titania.

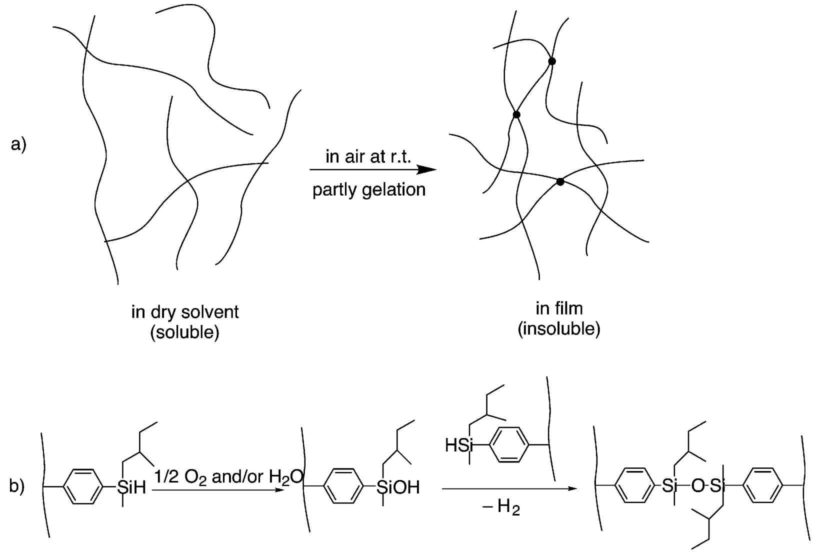

Figure 3. (a) Schematic gelation of polymer **1** and (b) a proposed reaction scheme at the cross-linking point (● Si−O−Si linkage).

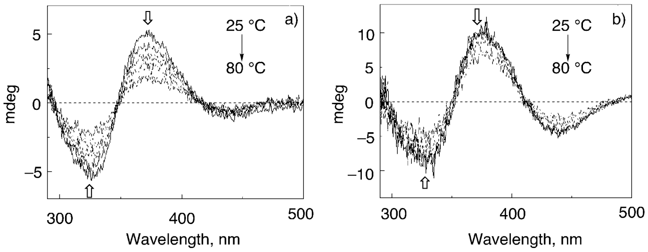

Figure 4. CD spectra of **1** (a) in toluene ($c = 1.1 \times 10^{-4}$ M) and (b) in the gel film (prepared from toluene solution of $c =$ 0.24 g/mL) measured in the temperature range from 25 to 80 °C.

Conclusion

We successfully synthesized and characterized a SiH-containing chiral poly(phenylacetylene) with no structural defects. This polymer readily turned into a gel film with Si−O−Si cross-linkages without evolution of volatiles by standing in air at room temperature. This polymer exhibited a quite large optical rotation and molar ellipticities in the backbone absorption region in toluene. The CD intensity of the chiral gel film hardly changed in the range from 25 to 85 °C, presumably due to Si−O−Si linkages. Organic−inorganic composites were easily obtained simply by stirring inorganic particles such as titania and silica gel in the polymer solution. These simple and clean Si−O−Si cross-linking reaction and surface-coating technique for preparing chiral polyacetylene-based gel film and organic−inorganic composites could be powerful synthetic tools to develop polarized optical/electronic devices based on chiral conjugated polymers[12] as well as new types of optical resolution membranes and chiral column-packing materials.

Experimental Section

Materials. Dichloromethylsilane (TCI Co., Ltd.), (*S*)-2-methylbutyl bromide (Aldrich, $[\alpha]^{21}$ +4.5 °, $c = 5$ in $CHCl_3$), and $[(nbd)RhCl]_2$ (Aldrich) were used as received. *p*-Bromophenylacetylene was prepared according to the literature.[13]

Synthesis of Monomer. *[(S)-2-Methylbutyl]methylchlorosilane (**2**).* A 500-mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and was flushed with dry nitrogen gas. Diethyl ether (150 mL) and dichloromethylsilane (5.9 mL, d 0.89, 57 mmol) were placed in the flask. The solution was cooled at −75 °C, to which (*S*)-2-methylbutylmagnesium bromide (57 mmol in 100 mL of diethyl ether) prepared beforehand was added dropwise under vigorous stirring. After completion of the addition, the mixture was stirred at that temperature for 1 h, then gradually warmed to room temperature, and kept overnight. The salts were removed by filtration of the reaction mixture through a sintered glass (G3) filled with Celite, and then diethyl ether was evaporated at room temperature. The crude product was purified by distillation to give the desired product (yield 3.6 g, 41%) as a colorless liquid. bp 135−138 °C/760 mmHg. ^1H NMR ($CDCl_3$, δ): 4.81 (hexet, 1H, Si*H*), 1.58−0.95 (m, 11H, $CH_2CH(CH_3)CH_2CH_3$), 0.52 (d, 3H, $SiCH_3$) ppm.

*p-[{(S)-2-Methylbutyl}methylsilyl]phenylacetylene (**3**).* A 200-mL round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen gas. *p*-Bromophenylacetylene (4.27 g, 23.6 mmol) and dry THF (100 mL) were placed in the flask at −75 °C. At the same temperature, a hexane solution of *n*-butyllithium (30.2 mL, 1.56 M, 47.2 mmol) was added dropwise, and the reaction mixture was stirred for 4 h. A solution of compound **2** (3.56 g, 23.6 mmol) in dry THF (30 mL) was added dropwise, and it was allowed to warm to room temperature slowly and kept overnight. After excess water was added to the reaction mixture, the stirring was continued for 1 h. The mixture was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (Merck, silica gel 60; eluent, hexane) to give the desired product (yield 2.2 g, 43%) as a colorless liquid. IR (KBr): 3300, 2959, 2818, 2780, 2170, 1103, 889 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.51−7.45 (m, 4H, aromatic), 4.39 (hexet, 1H, Si*H*), 3.10 (s, 1H, ethynyl), 1.39−0.60 (m, 11H, $CH_2CH(CH_3)CH_2CH_3$), 0.33 (d, 3H, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$, δ): 138.5, 134.1 131.2, 122.6, 83.7, 77.6, 32.6, 31.3, 22.0, 21.4, 11.4, −5.0 ppm. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 76.40; H, 9.56.

Synthesis of Polymer. *Poly[p-[{(S)-2-methylbutyl}methylsilyl]phenylacetylene] (**1**).* To a solution of monomer (0.22 g, 1.0 mmol) in dry toluene (1.0 mL) at 25 °C under nitrogen, a solution of $[(nbd)RhCl]_2$ (2.3 mg, 5.0 μmol) and Et_3N (10 μL) in dry toluene (1.0 mL) was added. The polymerization was kept at 25 °C for 1 h, and then the solution was dissolved in toluene (ca. 10 mL) and poured into a large excess of dry

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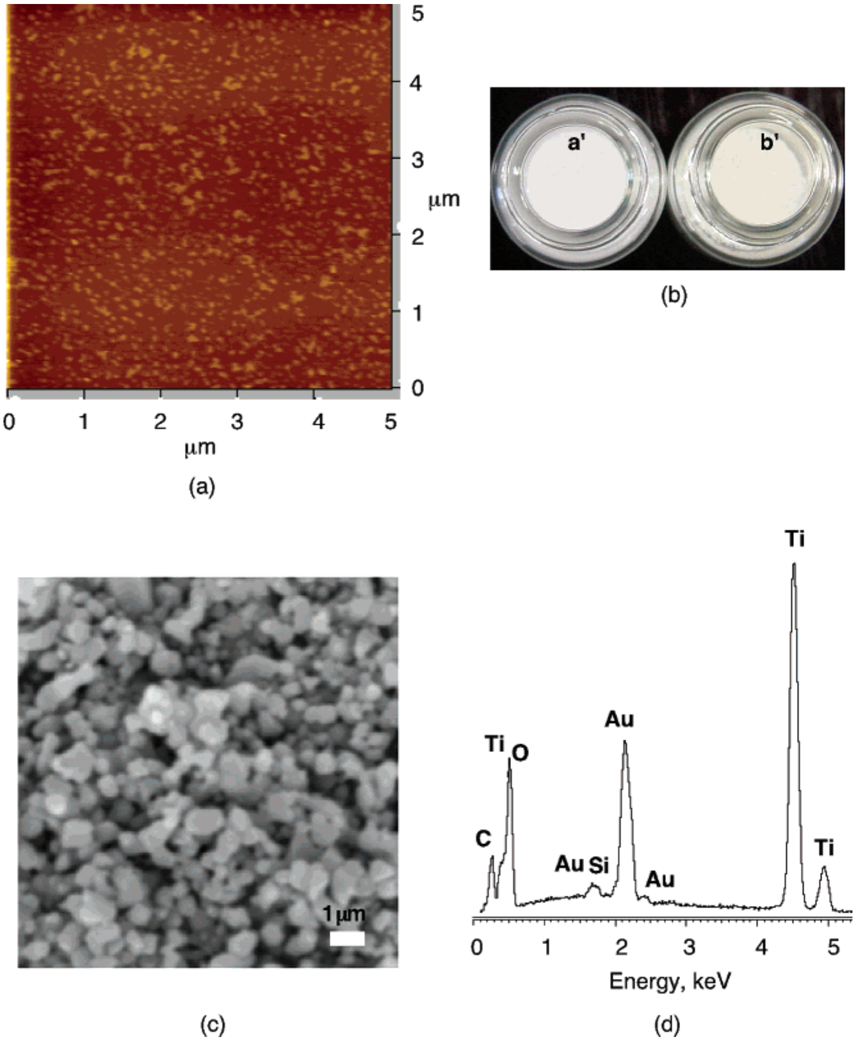

Figure 5. (a) AFM image of **1** on mica. (b) Colors of **a′**: silica gel and **b′**: silica gel coated with **1**. (c) SEM image and (d) EDX spectrum of titania particle coated with **1**. The sample was previously deposited with gold.

methanol to precipitate the polymer. The polymer was filtered with a sintered glass (G3) and dried in a nitrogen atmosphere and in a vacuum for a few minutes. Furthermore, to prevent gelation in air, the polymer was immediately dissolved in dry toluene to prepare a stock solution ($c = 12$ mg/mL). IR (film): 2959, 2818, 2780, 2170, 1180, 1110, 1103, 889 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.80−6.20 (b, 4H, aromatic), 5.82 (s, 1H, alkenylenic), 4.31 (s, 1H, Si*H*), 1.47−0.84 (b, 11H, $CH_2CH(CH_3)$-CH_2CH_3), 0.18 (s, 3H, $SiCH_3$) ppm. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 70.41; H, 8.96. The significant difference between the calculated and found values may be due to the fact that the SiH groups in the polymer thermally cross-link at relatively low temperature before decomposition.

Measurements. ^{1}H (400 MHz) NMR spectrum was measured in $CDCl_3$ solution at 25 °C on a JEOL EX-400 spectrometer. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymers were evaluated using gel permeation chromatography (Shimadzu A10 instruments, Polymer Laboratories, PLgel Mixed-B (300 mm in length) as a column and HPLC-grade tetrahydrofuran as eluent at 40 °C), based on a calibration with polystyrene standards. Optical rotation at the Na-D line was measured with a JASCO DIP-370 polarimeter using a quartz cell with a path length of 10 mm at room temperature. IR, UV−vis, and CD spectra were measured on Horiba FT-730, JASCO UV-550, and JASCO J-820 spectrophotometers, respectively. An AFM image was recorded on a Seiko SPI3800N atomic force microscope using a standard silicon probe with a 14 N/m spring constant in dynamic force mode. The morphologies of the titania coated with the polymer were imaged on an Hitachi S-3500N scanning electron microscope (SEM) operating at an accelerating voltage of 20 kV. Elemental analysis was determined using an Horiba EX-400 energy-dispersive X-ray (EDX) spectrometer attached to the microscope.

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