PAPER

Enhanced sol-gel polymerization of organoallylsilanes by solvent effect[†]

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We investigated solvent effects on the acid-catalyzed deallylation of organoallylsilane precursors to identify mild sol–gel polymerization conditions. Organoallylsilanes are expected to be alternative precursors for preparation of functionalized organosilica hybrids but they undergo sol–gel polymerization with difficulty due to their low reactivity towards hydrolysis. Sol–gel polymerization of model organoallylsilane precursors was conducted in various organic solvents and deallylation was monitored by ¹H NMR spectroscopy. The nature of the solvent was found to strongly influence the deallylation rate and a significant correlation was observed between reaction rate and solvent basicity, which suggests that proton activity is a key factor in enhancing the reaction rate. In particular, acetonitrile was found to most effectively enhance the rate, and it accelerated the formation of a spirobifluorene-bridged organosilica hybrid film from its allylsilane precursor under a mild acidic condition. This key finding can be generally utilized for the preparation of organoallylsilane-derived highly functionalized organosilica hybrids.

Introduction

Organosilica hybrid materials have received considerable attention in various research areas for their potential application in catalysts, adsorbents and optical devices.¹⁻³ These materials are readily prepared through sol-gel polymerization (hydrolysis and polycondensation) of organosilane precursors with hydrolyzable silyl groups (SiR_nX_{4-n}: X = OR', halide, OCOR', NR'₂, etc.)^{4,5} A broad spectrum of functional organic groups (R) has been incorporated into amorphous and ordered silicate frameworks alike.^{1-3,6-8} Recent demands for the development of highly functionalized organosilica hybrids necessitate the use of organosilane precursors having significant optical, chemical or electrical functionalities. However, synthesis of the desired precursors is often difficult, because the high reactivity of conventional silvl groups causes side reactions such as polymerization and decomposition during the silvlation reaction and purification. In particular, a serious problem is that silica gel chromatography cannot be utilized for purification of

"Toyota Central R&D Laboratories, Inc., Nagakute, Aichi, 480-1192, Japan. E-mail: inagaki@mosk.tytlabs.co.jp; Fax: +81-561-63-6507; Tel: +81-561-71-7393 conventional organosilane precursors, unlike for general organic compounds.

Recently, allylsilyl groups (Si-CH₂CH=CH₂) have been found to behave as a synthetic equivalent to conventional silvl groups.⁹⁻¹⁵ Allylsilyl groups can be hydrolyzed and condensed under acidic hydrolytic conditions through the elimination of propene (deallylation) (Scheme 1).9,16-18 They have a good tolerance for cross-coupling reaction conditions and silica gel chromatography,¹⁹ and thus are expected to be an alternative source of hydrolyzable silyl groups for synthesis of complex organosilane precursors.¹⁹ Recently, we also reported on a new organoallylsilane precursor containing spirobifluorene as a bridging group, which underwent acidic sol-gel polymerization to form a periodic mesoporous organosilica (PMO) film.²⁰ However, allylsilyl groups are generally less reactive to hydrolysis than conventional silvl groups, and thus high acid concentrations (e.g. 0.2 M hydrochloric acid (HCl) in THF) and high temperatures (e.g. 60 °C) are usually required for hydrolysis in organic solvents compared to those for organoalkoxysilanes





Scheme 1 Presumed deallylation mechanism of an allylsilyl group during acid-catalyzed hydrolysis and polycondensation.

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(*e.g.* 0.01 M HCl at rt).¹⁴ This is likely to cause decomposition of bridging organic groups and/or undesired Si–C bond cleavage between the silyl group and the bridging-organic group.^{21,22} Thus it is of great importance to identify mild conditions for sol–gel polymerization of organoallylsilane precursors.

In this paper, we investigate the effects of solvents on the acidcatalyzed deallylation of organoallylsilane precursors to identify mild conditions for sol–gel polymerization. Hydrolysis and polycondensation of model precursors were conducted in various organic solvents and the deallylation behaviors were monitored by ¹H NMR spectroscopy. The nature of the solvent strongly influenced the reaction rate and the observed solvent effect was well explained in terms of the solvent basicity parameter (solvent basicity: SB), which suggests that the proton activity is a key factor in enhancing the reaction rate. The use of a solvent with low SB was confirmed to accelerate the formation of a functional organosilica hybrid film from its allylsilane precursor under a mild acidic condition.

Results and discussion

Sol-gel polymerization behavior of model organoallylsilane precursors by ¹H NMR spectroscopy

The behavior of organoallylsilanes under acid-catalyzed hydrolysis and polycondensation was examined in various organic solvents containing HCl (0.2 M in the solutions). Organoallylsilanes 1a and 1b (Fig. 1) were used as model precursors because both diallylethoxy- and triallyl-silyl groups have been utilized as precursors for PMO synthesis.14,20 Water-soluble polar solvents, methanol (MeOH), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), acetone and acetonitrile (MeCN) were chosen because they were appropriate for preparing a homogeneous solution containing the organoallylsilane, HCl and water. Solutions of 1a and 1b were stirred at 60 °C for 3-48 h and subjected to hydrolysis and polycondensation to obtain sol solutions. The sol solutions were cast on a glass substrate in order to check whether a solid film was obtained (Table 1). Conversion of the allyl groups in the organoallylsilane precursors during the reactions was monitored by ¹H NMR spectroscopy (signals from the β -hydrogens of the allylsilyl groups, Fig. 3 and S1–S6 in the ESI[†]) in deuterated solvents.

Fig. 2a plots the conversion of allyl groups in **1a** in various solvents after the addition of HCl, and Table 1 gives the deallylation rates (v_0) at the initial 0.5 h.²³ The v_0 was strongly influenced by the solvent. The highest v_0 of 4.53×10^{-4} M s⁻¹ was obtained with MeCN, which gave complete deallylation within 3 h (Fig. 3a). The second highest v_0 of 8.64×10^{-5} M s⁻¹ was obtained with acetone, which gave 76% deallylation after 4 h (Fig. 3b). These solutions (MeCN and acetone) released considerable amounts of a gas during the reaction, which was



Fig. 1 Chemical structures of model organoallylsilane precursors 1a and 1b.

Table 1 Acidic sol-gel polymerization of model organoallylsilane precursors 1a and 1b in various organic solvents^{*a*}

Entry	Precursor	Solvent	$v_0^{\ b}/M \ s^{-1}$	Solid film formation
1	1a	MeOH	2.40×10^{-5}	No
2		THF	2.14×10^{-5}	No
3		DMSO	0.90×10^{-5}	No
4		Acetone	8.64×10^{-5}	Yes $(24 h)^c$
5		MeCN	4.53×10^{-4}	Yes $(3 h)^c$
6	1b	Acetone	1.23×10^{-5}	No
7		MeCN	3.88×10^{-5}	Yes $(4 h)^c$
6 7	1b	Acetone MeCN	1.23×10^{-5} 3.88×10^{-5}	No Yes (4 h) ^c

^{*a*} Reactions of the allylsilane precursors **1a** and **1b** (0.10 mmol) were carried out at 60 °C for 3–48 h in the solvents (0.25 mL) in the presence of HCl (0.2 M). ^{*b*} The deallylation rate at the initial 0.5 h. ^{*c*} The reaction time required for the formation of a solid organosilica film from the sol-solution.



Fig. 2 Conversion of allyl groups in (a) **1a** and (b) **1b** with the reaction time for the sol solutions using various deuterated solvents. Solvents are labelled as follows: MeCN (\bigcirc); acetone (\triangle); MeOH (\diamond); THF (\square); and DMSO (×) for **1a**, MeCN (\bigcirc) and acetone (\blacktriangle) for **1b**.

identified as propene by ¹H NMR spectroscopy (Fig. S7 in the ESI[†]). Solid films were formed from the sol solutions after stirring in MeCN and acetone for 3 h and 24 h, respectively, to allow evaporation of the solvents (Table 1, entries 4 and 5). In MeCN, a solid film was also obtained even at a HCl concentration



Fig. 3 Changes in the ¹H NMR spectra (signals from the β -hydrogens of the allylsilyl groups) of the sol solutions of **1a** in (a) MeCN- d_3 , (b) acetone- d_6 and (c) DMSO- d_6 after the addition of HCl.

ten-fold lower (0.02 M) than that used for the other solvents after 30 h. These results indicate that the polycondensation reaction was significantly promoted in MeCN. In contrast, the use of MeOH, THF and DMSO resulted in relatively low v_0 of 2.40 × 10^{-5} , 2.14 × 10^{-5} and 0.90 × 10^{-5} M s⁻¹, respectively (Table 1, entries 1–3). For example, more than 90% of the allyl groups remained after 4 h in DMSO (Fig. 3c). For these solvents, the sol solutions formed soluble gel-like films even after stirring for 120 h. On the other hand, the ethoxy group in **1a** was found to be completely hydrolyzed to ethanol within 10 min regardless of the solvent (Fig. S1–S5 in the ESI†). This surely indicates that hydrolysis of the ethoxysilyl group is very fast compared to that of the allylsilyl group and deallylation determines the overall sol–gel polymerization rate of **1a**.

Fig. 2b plots the conversion of allyl groups in **1b** in MeCN and acetone. The v_0 of **1b** is higher for MeCN (3.88×10^{-5} M s⁻¹) than acetone (1.23×10^{-5} M s⁻¹), which was a similar result to that observed for **1a**. On the other hand, the deallylation rates of **1b** were smaller than those of **1a** due to the lower reactivity of the triallylsilyl group (Table 1, entries 6 and 7). However, despite the low reactivity, the sol-solution of **1b** in MeCN formed a solid film after stirring for 4 h.

Mechanism of solvent effect on sol-gel polymerization of organoallylsilane precursors

In the following we outline the origin of the observed solvent effect based on the underlying reaction mechanism. Hydrolysis and polycondensation of the allylsilyl groups are considered to proceed as follows: (i) electrophilic addition of a proton to the allyl group forms a β -silyl cation intermediate A and (ii) subsequent nucleophilic attack of water to A forms a silanol species along with the generation of propene (Scheme 1a). The silanol species then further reacts with A (or another silanol species) to form a siloxane bond, allowing polycondensation to progress (Scheme 1b). According to this scheme, the deallyation reaction can be influenced by three factors: (i) proton activity, (ii) stability of the β -silyl cation intermediate and (iii) nucleophilicity of the water (or silanol species). These factors are closely related to the Catalán solvent basicity (SB),²⁴ dielectric constant $(D_C)^{25}$ and Gutmann's acceptor number (AN), respectively.²⁶ Here, the SB is an index for hydrogen-bond acceptor basicity and a low SB leads to a high proton activity, accelerating electrophilic addition of the proton to the allyl group. $D_{\rm C}$ is an index for solvent polarity and a high $D_{\rm C}$ leads to high stability of the cationic intermediate A, decreasing the activation barriers of both steps. AN is an index for the strength of the solvent as a Lewis acid and a low AN leads to high nucleophilicity of the oxygen atoms in water (or the silanol species), accelerating the nucleophilic attack step. Fig. 4ac show the relationship between the initial deallylation rate v_0 of 1a and SB, $D_{\rm C}$, and AN, respectively, for various solvents. A correlation was apparent for v_0 vs SB, but not for v_0 vs D_C or v_0 vs AN. The strong SB-dependence of v_0 was further supported by additional experiments using N,N-dimethylformamide and 2,2,2-trifluoroethanol as a solvent in which the polymerization reaction of 1a proceeds in the solvents with low SB, regardless of the values of their $D_{\rm C}$ and AN (Sections 3 in the ESI[†]). The v_0 was also correlated to Gutmann's donor number²⁶ (an index of Lewis basicity) but not to Dimroth-Reichardt's E_T^N value²⁷



Fig. 4 Relationship between the initial deallylation rate (v_0) of **1a** and (a) solvent basicity (SB), (b) dielectric constant (D_C) or (c) acceptor number (AN) for various solvents. Solvents are labelled as follows: MeCN (\bigcirc); acetone (\triangle); MeOH (\diamond); THF (\square); and DMSO (×).

(an index of solvent polarity) (Fig. S9[†]). These results suggest that the present strong solvent effect results from differences in the proton activities in the solvents. This may also suggest that electrophilic addition of a proton is the rate-determining step in the deallylation reaction, which is reasonable since this step was found to be slow in other electrophilic substitution reactions of allylic silanes.¹⁷

Preparation of spirobifluorene-bridged organosilica film under a mild sol-gel polymerization condition

The solvent effect was also confirmed for highly functional spirobifluorene-bridged allylsilane precursor SBF-Si (Fig. 5). In a previous report, SBF-Si underwent hydrolysis and polycondensation in the presence of a surfactant under a highly acidic condition (e.g. 0.2 M HCl in THF) to yield a highly emissive PMO film.²⁰ Here, we carried out sol-gel polymerization of SBF-Si in a mixed solvent of THF/MeCN (2:1) and in pure THF at an acid concentration ten-fold lower (0.02 M HCl) without a surfactant. The sol solution of THF/MeCN formed a solid film after stirring for 3 h, whereas the sol solution of pure THF did not form a solid film even after stirring for 24 h. Fig. 6 shows UVvis absorption and fluorescence emission spectra of the obtained spirobifluorene-silica hybrid film. The film shows absorption bands at 364 and 378 nm and exhibits strong blue emission bands at 448 and 470 nm with a total fluorescence quantum yield of 0.50 (excited at 360 nm). These optical properties were largely similar to those of a previously reported PMO film prepared under a strong acidic condition.²⁰ These results suggest that the solvent



Fig. 5 Chemical structure of spirobifluorene-bridged allylsilane precursor SBF-Si.



Fig. 6 UV-vis absorption (\bullet) and fluorescence emission (\bigcirc , excited at 360 nm) spectra of the spirobifluorene-bridged organosilica film.

effect can be generally applied to the preparation of highly functional organosilica hybrid materials from a variety of functional and stable organoallylsilane precursors.

Conclusions

In summary, we identified a significant solvent effect on the acidcatalyzed deallylation of organoallylsilane precursors and in mild sol–gel polymerization conditions. The observed solvent effect was well explained in terms of SB but not the D_C or AN of the solvent. These results suggest that proton activity is a key factor in enhancing the reaction rate. In particular, MeCN was found to most effectively enhance the rate, and accelerated sol–gel polymerization of **SBF-Si** to form a highly emissive spirobifluorenesilica hybrid film under a mild acidic condition. This key finding can be generally utilized for the preparation of a variety of organoallylsilane-derived highly functionalized organosilica hybrids.

Experimental

Materials

All reactions were carried out under argon using standard high vacuum and Schlenk techniques. Unless otherwise noted, all materials, including dry solvents, were purchased from commercial suppliers (Sigma-Aldrich, Tokyo Chemical Industry, Wako Pure Chemical Industries and AZmax Co., Ltd) and used without further purification. **SBF-Si** was prepared according to a literature method.²⁰

General methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-EXC400P spectrometer (400 MHz for ¹H and 100 MHz for ¹³C). Chemical shifts are reported in δ ppm referenced to an internal SiMe₄ standard for ¹H NMR and chloroform-*d* (δ 77.0) for ¹³C NMR, respectively. Mass spectra were recorded on a Waters GCT PremierTM mass spectrometer (FI: field ionization). Ultraviolet-visible (UV-vis) absorption spectra were measured using a Jasco V-670 spectrometer. Fluorescence emission spectra were obtained using a Jasco FP-6500 spectrometer. Fluorescence quantum yields were determined using a photoluminescence quantum yield measurement system equipped with a calibrated integrating sphere (Hamamatsu Photonics, C9920-02).

Synthesis

Diallyl(ethoxy)(p-tolyl)silane (1a). To a solution of triethoxy (p-tolyl)silane (12.0 g, 47.2 mmol) in dry Et₂O (20 mL) was added dropwise a solution of allylmagnesium bromide (142 mL, 1.0 M in Et₂O, 142 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 24 h and quenched with saturated NH₄Cl solution and extracted with Et₂O. The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica; hexanes) affording the title compound as a colorless oil (9.94 g, 86%). $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si) 1.20 (3H, t, J 6.8 Hz, -OCH₂CH₃), 1.93 (4H, ddd, J 8.0 Hz, 1.2 Hz, 0.8 Hz, -SiCH₂CH=CH₂), 2.36 (3H, s, -CH₃), 3.75 (2H, q, J 6.8 Hz, -OCH₂CH₃), 4.90 (2H, ddt, J 10.0 Hz, 1.4 Hz, 0.8 Hz, -SiCH₂CH=CH₂), 4.95 (2H, ddt, J 16.0 Hz, 1.4 Hz, 1.2 Hz, -SiCH₂CH=CH₂), 5.82 (2H, ddt, J 16.0 Hz, 10.0 Hz, 8.0 Hz, -SiCH₂CH=CH₂), 7.20 (2H, d, J 7.8 Hz, aromatic), 7.47 (2H, d, J 7.6 Hz, aromatic); $\delta_{\rm C}$ (100 MHz; CDCl₃; CDCl₃) 18.4, 21.3, 21.5, 59.2, 114.6, 128.6, 131.4, 133.3, 134.1, 139.8; m/z (FI) 246.1430 (M⁺. C₁₅H₂₂OSi requires 246.1440).

Triallyl(p-tolyl)silane (1b). To a solution of (p-tolyl)trichlorosilane (2.40 g, 10.6 mmol) in dry Et₂O (30 mL) was added dropwise a solution of allylmagnesium bromide (40 mL, 1.0 M in Et₂O, 40 mmol) at 0 °C. The reaction mixture was refluxed for 16 h, quenched with saturated NH₄Cl solution and extracted with Et₂O. The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica; hexanes) affording the title compound as a colorless oil (2.46 g, 95%). δ_H (400 MHz; CDCl₃; Me₄Si) 1.85 (6H, ddd, J 8.2 Hz, 1.2 Hz, 0.8 Hz, -SiCH₂CH=CH₂), 2.35 (3H, s, -CH₃), 4.88 (3H, ddt, J 10.4 Hz, 1.6 Hz, 0.8 Hz, -SiCH₂CH=CH₂), 4.91 (3H, ddt, J 16.0 Hz, 1.6 Hz, 1.2 Hz, -SiCH₂CH=CH₂), 5.79 (3H, ddt, J 16.0 Hz, 10.4 Hz, 8.2 Hz, -SiCH₂CH=CH₂), 7.18 (2H, d, J 8.0 Hz, aromatic), 7.41 (2H, d, J 8.0 Hz, aromatic); $\delta_{\rm C}$ (100 MHz; CDCl₃; CDCl₃) 19.6, 21.5, 114.2, 128.6, 131.5, 134.0, 134.3, 139.3; m/z (FI) 242.1493 (M⁺. C₁₆H₂₂Si requires 242.1491).

Observation of sol-gel polymerization of model organoallylsilane precursors by ¹H NMR measurements

Precursor **1a** (25 mg, 0.10 mmol) was dissolved in MeOH- d_4 , THF- d_8 , DMSO- d_6 , acetone- d_6 or MeCN- d_3 (0.25 mL), respectively. Precursor **1b** (25 mg, 0.10 mmol) was dissolved in acetone- d_6 or MeCN- d_3 (0.25 mL), respectively. As an internal standard, a small amount of 1,4-dichlorobenzene or naphthalene was added to the precursor solution. To calculate the initial concentration of the allyl group relative to the internal standard, a reaction aliquot was measured by ¹H NMR spectroscopy before the reaction. Then 2 M HCl aqueous solution was added (2.5–25 μ L, 5.0–50 μ mol, 0.02–0.2 M in reaction solvent), and the reaction mixture stirred at 60 °C. The sol solution was cast on a glass plate to determine whether a solid organosilica film could be obtained. The reaction aliquot (25 μ L) was also rapidly

diluted with the same deuterated solvent and quickly measured by ¹H NMR spectroscopy. Conversion of the allyl and ethoxy groups was determined by integrating the selected resonance peaks for the allyl and ethoxy groups, respectively, relative to that of the internal standard.

Preparation of spirobifluorene-bridged organosilica film

Spirobifluorene-bridged allylsilane precursor **SBF-Si** (10 mg, 7.5 μ mol) was dissolved in THF/MeCN (2 : 1 = v/v, 0.40 mL) and then 2 M HCl aqueous solution (4.0 μ L, 8.0 μ mol, 0.02 M in reaction solvent) was added to the solution. The mixture was stirred at 60 °C for 3 h. The sol solution was diluted with THF (1.20 mL), coated on a quartz glass plate by spin-coating (4000 rpm, 30 s) and dried under reduced pressure to give an organosilica film.

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