Enhanced sol-gel polymerization of organoallylsilanes by solvent effect

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1. Observation of sol-gel polymerization behaviors of 1a and 1b by \(^1\)H NMR spectroscopy

\[ \begin{array}{c}
\text{H}_3C-\text{C}=\text{C}-\text{Si}-\text{R} \\
\text{H}^a & \text{H}^b & \text{H}^c & \text{H}^d
\end{array} \]

\[ \xrightarrow{2 \text{ M HClaq}} \]

\[ \text{inner standard} \quad \text{deuterated solvent} \quad 60^\circ \text{C} \]

\[ \xrightarrow{\text{1-Oligomer}} \]

\[ \begin{array}{c}
\text{H}_3C-\text{C}=\text{C}-\text{Si}-\text{OH} \\
\text{H}^a & \text{H}^b & \text{H}^c & \text{H}^d
\end{array} \]

\[ + \quad \text{CH}_3 \quad \text{↑} \quad + \quad \left( \begin{array}{c}
\text{H}_3C-\text{C}=\text{C}-\text{OH} \\
\text{H}^a & \text{H}^b & \text{H}^c & \text{H}^d
\end{array} \right) \]

**Scheme S1** Acid-catalyzed sol-gel polymerization of 1a and 1b. The protons H\(^a\), H\(^b\), H\(^c\) and H\(^d\) were monitored by \(^1\)H NMR spectroscopy.

Conversion of the allyl groups in the organoallylsilane precursors 1a and 1b during the reactions was monitored by \(^1\)H NMR spectroscopy. The measurements were carried out for their sol-solutions containing internal standards (1,4-dichlorobenzene: DCB or naphthalene: Nap). Figs. S1-S6 show the \(^1\)H NMR spectra of 1a or 1b in various deuterated solvents at 0 min, 10 min and 4 h after the addition of HCl. In the figures, the letters (a, b, c, and d) indicate the signals corresponding to the protons shown in Scheme 1.

For 1a, the signals corresponding to the proton b completely disappeared along with the appearance of the signals corresponding to the proton d within 10 min for all the solvents (Figs. S1-S5), which indicates that the ethoxy group in 1a is immediately converted to ethanol regardless of the nature of solvents. In contrast, the nature of solvents strongly affected the deallylation rate of 1a. After 4 h, intensities of the signals corresponding to the proton a decreased by 100% for MeCN (Fig. S1), 76% for acetone (Fig. S2) and less than 30% for MeOH, THF, and DMSO (Figs. S3-S5). Weak signals at the similar positions after 4 h for MeCN were identified as the proton c of propene dissolved in the solvents.

MeCN was also effective for deallylation of 1b and the signals corresponding to the proton a completely disappeared within 4 h (Fig. S6a). Meanwhile, 80% of the allyl groups remained after 4 h for acetone (Fig. S6b).
Fig. S1 $^1$H NMR spectra of the sol-solution of 1a in MeCN-$d_3$ at 0 min, 10 min and 4 h after the addition of HCl.

Fig. S2 $^1$H NMR spectra of the sol-solution of 1a in acetone-$d_6$ at 0 min, 10 min and 4 h after the addition of HCl.
Fig. S3 $^1$H NMR spectra of the sol-solution of 1a in MeOH-$d_4$ at 0 min, 10 min and 4 h after the addition of HCl.

Fig. S4 $^1$H NMR spectra of the sol-solution of 1a in THF-$d_8$ at 0 min, 10 min and 4 h after the addition of HCl.
Fig. S5 $^1$H NMR spectra of the sol-solution of 1a in DMSO-$d_6$ at 0 min, 10 min and 4 h after the addition of HCl.

Fig. S6 $^1$H NMR spectra of the sol-solutions of 1b in (a) MeCN-$d_3$ and (b) acetone-$d_6$ at 0 min and 4 h after the addition of HCl.
2. Identification of the generated gas during sol-gel polymerization of 1a and 1b

\[
\text{1a or 1b} \xrightarrow{2 \text{ M HCl aq}} \text{(MeCN, 60 °C, 1 h)} \rightarrow \text{1-Oligomer} + \text{propene}
\]

Scheme S2 Generation of propene during acid-catalyzed sol-gel polymerization of 1a and 1b.

The generated gas during acid-catalyzed sol-gel polymerization of 1a and 1b was identified by \(^1\)H NMR spectroscopy (Scheme S2). A 50 mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar was sequentially charged with 1a or 1b (250 mg, 1.0 mmol) and MeCN (2.5 mL). After addition of a 2 M HCl aqueous solution (0.25 mL, 0.50 mmol), the flask was capped with a septum and stirred at 60 °C for 1 h (Caution!: the increased inner pressure may blow out the septum). The gas phase in the flask was collected with a syringe and passed through MeCN-\(d_3\). The solution was immediately characterized by \(^1\)H NMR spectroscopy (Fig. S1). The generated gas was identified as propene.\(^1\)

\(^1\)H NMR (400 MHz, MeCN-\(d_3\)) \(\delta\) 1.70 (ddd, \(J = 6.4 \text{ Hz, 1.7 Hz, 1.4 Hz}, 3\)H), 4.93 (ddq, \(J = 10.1 \text{ Hz, 2.2 Hz, 1.4 Hz}, 1\)H), 5.04 (ddq, \(J = 16.6 \text{ Hz, 2.2 Hz, 1.7 Hz}, 1\)H), 5.85 (ddq, \(J = 16.6 \text{ Hz, 10.1 Hz, 6.4 Hz}, 1\)H).

Fig. S7 \(^1\)H NMR spectrum of the generated gas dissolved in MeCN-\(d_3\).
3. Sol-gel polymerization of 1a in other organic solvents

We investigated the sol-gel polymerization behaviors of 1a in other organic solvents to further confirm that SB rather than $D_C$ or AN is the key factor of the reaction. N,N-dimethylformamide (DMF; SB: 0.614, $D_C$: 35.9, AN: 16.0) and a mixed solvent of 2,2,2-trifluoroethanol (TFE; SB: 0.107, $D_C$: 26.7, AN: 53.3)/THF (10:1) were newly selected and the sol-gel polymerization were carried out under 0.2 M HCl concentration for this purpose. The use of DMF did not form a solid organosilica film from the sol solution of 1a even after stirring for 24 h. In contrast, the use of TFE/THF formed a solid organosilica film after stirring for only 1 h.

These experimental results and relationship between the SB and $D_C$ or AN value were plotted, respectively (Fig. S8). As shown in Figs. S8a and S8b, the use of low SB solvents was found to be effective for the reaction regardless of $D_C$ and AN values (MeCN vs DMF or THF, and TFE/THF vs MeCN). In addition, it should be noted that the use of high SB solvents is ineffective for the reaction regardless of $D_C$ and AN values (DMF, MeOH and THF). These results clearly indicate that that SB is the key factor of the reaction rather than $D_C$ or AN.

![Fig. S8](image)

**Fig. S8** Plots of (a) $D_C$ and (b) AN vs. SB for DMF, TFE, MeCN, MeOH and THF. “Yes (X h)” and “No (X h)” denotes whether a solid organosilica film was formed or not from the sol solutions of 1a using the corresponding solvents after stirring for X h.
4. Relationship between initial deallylation rate $v_0$ of 1a and other solvent parameters

The initial deallylation rate $v_0$ of 1a was plotted against Gutmann’s donor number (DN: an index of Lewis basicity)$^2$ and Dimroth-Reichardt’s $E_T^N$ value (an index of solvent polarity)$^3$ (Fig. S9) in addition to Catalán solvent basicity (SB), dielectric constant ($D_C$) and Gutmann’s acceptor number (AN) (Fig. 4 in the main text). Apparent correlation was observed for $v_0$ vs DN, but not for $v_0$ vs $E_T^N$ value.

![Graphs showing relationships between initial deallylation rate ($v_0$) and solvent parameters](image)

**Fig. S9** Relationships between the initial deallylation rate ($v_0$) of 1a and (a) Gutmann’s donor number (DN) or (b) Dimroth-Reichardt’s $E_T^N$ value. Solvents were labelled as follows: MeCN (○); acetone (△); MeOH (◇); THF (□); and DMSO (×).

5. References

