# Chemical Degelation of Polysilane Organogel by Selective Scission of Silicon Main Chain by Fluoride Anion

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Selective scission of the positively charged main chain of polydialkylsilane using tetrabutylammonium fluoride was utilized for facile chemical degelation of polymer-based organogel. The degelation mechanism was characterized by combinational analyses with photodiode array-equipped size exclusion chromatography, GC/MS, and FTIR measurements.

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Polymer-based organogelators have attracted much attention due to their potential uses for various applications, including chemo-mechanical, shock absorbing, drug delivering, and volatile organic compound (VOC) recycling materials.[1–5] Unlike small molecular organogelators, the polymer-based organogelators are easy to gelate without heating or sonication, also exhibiting long durability without precipitation. However, once such gelators form organogel, it is difficult to degelate, that is, to untangle covalently cross-linked polymer networks. In some cases, this limits applications of the polymer-based organogels.

Aiming for development of chemically degelable polymer-based organogel with a simple, moderate, and quick reaction, we focused on a silicon-catenated linear polymer, polydialkylsilane, PSi**1** (Figure 1a), on the basis of the following reasons; recently, Kawabe et al. demonstrated that, utilizing the difference in reactivity of dichlorosilanes with various alkyl side chains, block-like PSi**1** with random-coiled PSi**3** and semiflexible PSi**4** segments can be produced by the simultaneous Wurtz-type condensation copolymerization of dichloromethyl(3,3,3-trifluoropropyl)silane and dichlorodecyl(isobutyl)silane.[6] Here the block-copolymer nature of PSi**1** was determined by the selective scission of the Si main chain of PSi**3** segments with tetrabutylammonium fluoride (TBAF). Number-averaged molecular weight ($M_n$) of PSi**3** and PSi**4** segments of PSi**1** were estimated to be 2600 and 6000, respectively. Such segment selective scission may be initiated by an electrostatic interaction between a fluoride anion, $F^-$, and the positively charged Si main chain resulting from a strong electron-withdrawing 3,3,3-trifluoropropyl group. Furthermore, PSi**1** exhibited gelation ability with a variety of organic solvents with wide ranges of dielectric constants from 1.84 (*n*-pentane) to 7.58 (tetrahydrofuran, THF).[7,14] The key to gelation was an adequate combination of relatively stiff main chain and noncovalent cross-linkages, such as weak intra/interchain interactions among Si main chains and fluorine in the 3,3,3-trifluoropropyl groups, and van der Waals interactions among long alkyl side chains. Here we expected that the selective scission of the PSi**3** main chain would be applicable to chemical degelation of the polysilane organogel.

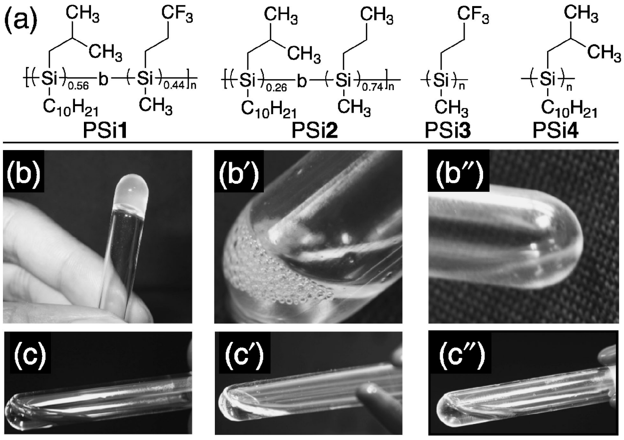


**Figure 1.** (a) Chemical structures of polysilanes, PSi**1**: poly[(isobutyl-*n*-decylsilane)$_{0.56}$-*b*-(methyl-3,3,3-trifluoropropylsilane)$_{0.44}$], PSi**2**: poly[(isobutyl-*n*-decylsilane)$_{0.26}$-*b*-(methyl-*n*-propylsilane)$_{0.74}$], PSi**3**: poly(methyl-3,3,3-trifluoropropylsilane), and PSi**4**: poly(isobutyl-*n*-decylsilane). (b) Photographs of 10 wt % PSi**1** dissolved in toluene after 12 h at room temperature. After 10-min (b′) and 15-min addition of tetrabutylammonium fluoride (TBAF) (b″). (c) Photographs of PSi**2** prepared under the same conditions as PSi**1**. After 10-min (c′) and 15-min addition of TBAF (c″). $F^-$ (mol)/Si repeat unit (mol): 0.5.

PSi**1** organogel was prepared as described in a previous paper.[7,14] Briefly, PSi solutions (10 wt %) were prepared in toluene at room temperature, and kept in the dark. After 12 h, PSi**1** became a translucent gel (Figure 1b). To initiate the degelation, 10-μL TBAF (1.0 M/THF, $F^-$ (mol)/Si repeat unit (mol): 0.5) was added. Upon addition of TBAF, bubbles immediately came out from the PSi**1** gel (Figure 1b′). The foam gradually receded, resulting in a low viscosity solution (sol) within 15 min (Figure 1b″). On the other hand, PSi**2** with *n*-propyl instead of 3,3,3-trifluoropropyl groups, did not exhibit gelation but became a viscous solution (Figure 1c) even following the same procedure as that of PSi**1**, resulting from a lack of noncovalent cross-linkages among the Si main chain and 3,3,3-trifluoropropyl groups. Furthermore, the PSi**2** solution did not foam upon addition of TBAF (Figures 1c′ and 1c″) because TBAF can only cleave the positively charged Si–Si bonds of PSi**3** segments. Using size exclusion chromatography (SEC) with a photodiode array (PDA) detector, number-averaged molecular weight ($M_n$), polydispersity index (*PDI*), and conformations of PSi**1** were simultaneously evaluated. The detailed data are summarized in Table 1. PSi**1** originally showed a monomodal peak 1 at ca. 7.8 min. Upon addition of TBAF, four peaks appeared at (peak 2) 8.2, (3) 10.0, (4) 10.7, and (5) 11.4 min retention time (Figure 2B). Here the $M_n$ values at peak 3 and 4 were in similar

**Table 1.** Polymer data of PSi**1** before/after TBAF addition estimated from the SEC trace in Figure 2B

| | Peak 1 | Peak 2 | Peak 3 | Peak 4 | Peak 5 |
|---|---|---|---|---|---|
| $M_n$ ($\times 10^{-3}$)[a] | 281.6 | 459.8 | 18.9 | 4.2 | 1.1 |
| *PDI* | 5.5 | 1.9 | 1.1 | 1.1 | 1.1 |

[a] THF, polystyrene standard.

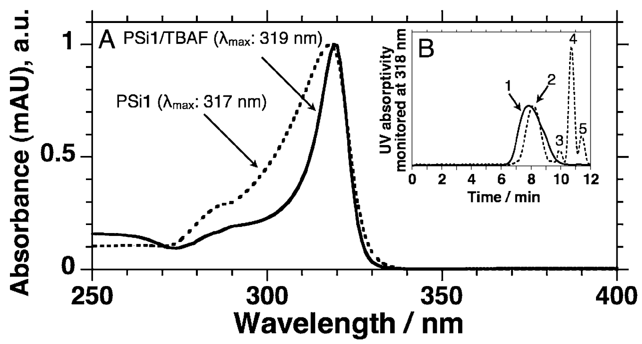


**Figure 2.** (A) UV absorption signal of **PSi1** detected with photodiode array-equipped size exclusion chromatography (SEC) before (dotted) and after 15-min addition of TBAF (solid). (B) SEC traces of **PSi1** before (solid) and after addition of TBAF (dotted).

ranges to those of **PSi3** and **PSi4** segments in **PSi1**. Considering that positively charged **PSi3** segments were selectively cleaved with TBAF, these signals may originate from the remaining **PSi4** segments through degradation of **PSi1** with TBAF, as described below.

Using UV absorption of PSi monitored with a PDA detector-equipped SEC, changes in global conformation of **PSi1** on TBAF addition were characterized (Figure 2A). Generally, global conformations of chain-like polymers, such as random-coiled or semiflexible, are classified with the values of viscosity index ($\alpha$), but measuring the viscosity index is complicated. In the case of polydialkylsilane, utilizing a clear relationship between $\alpha$ and the full width at half-maximum (*fwhm*), their global conformations can be easily evaluated.[8] Thus, the *fwhm* values decrease exponentially as a function of the value of $\alpha$. Here the UV absorption signals were monitored at 318 nm, originating from $\sigma_{\mathrm{Si}}$–$\sigma_{\mathrm{Si}}{}^*$ transition of the Si main chain. The *fwhm* value of **PSi1** was obtained to be 2207 $\mathrm{cm^{-1}}$, reflecting the block copolymer nature of PSi with random-coiled **PSi3** (4840 $\mathrm{cm^{-1}}$) and semiflexible **PSi4** (840 $\mathrm{cm^{-1}}$).[6] After TBAF addition, the *fwhm* values became narrower (1147 $\mathrm{cm^{-1}}$). This result further supports that only **PSi3** segments were selectively cleaved, whereas semiflexible **PSi4** segments remained. The resulting low viscosity solution was further characterized with FT-IR measurements.[9] Consequently, asymmetric stretching of SiOH at ca. 1080 $\mathrm{cm^{-1}}$ was significantly increased through degelation, instead of SiF ($\nu_{\mathrm{SiF}}$: 1000–800 $\mathrm{cm^{-1}}$) and SiH ($\nu_{\mathrm{SiH}}$: 2250–2100 $\mathrm{cm^{-1}}$) (Figure 3B). Thus, SiF or SiH terminal groups of the cleaved **PSi3** segments may be transformed to SiOH by hydrolysis with residual water in solvents.

Here we propose a selective cleavage mechanism of **PSi3** with TBAF, as follows (Scheme 1); first, the positively charged Si main chain of **PSi3** is cleaved by TBAF, to give **PSi3** segments with SiF and silyl anion termini (Step 1).[10] Subsequently, the silyl anion subtracts hydrogen from the $\beta$ position in the 3,3,3-trifluoropropyl side chain, followed by generation of trifluoropropene (Step 2).[11] This was supported by GC/MS measurements. Thus, an apparent peak was observed at $m/z$: 96, corresponding to trifluoropropene (Figure 3A). Here, the peak at $m/z$: 56 appeared to be $n$-butene because TBAF is known to easily decompose to tetrabutylammonium bifluoride, tributylamine, and 1-butene through Hofmann degradation.[12] Indeed, from $^{19}$F NMR measurement of TBAF, characteristic peaks of bifluoride were detected at −150.0 and −157.3 ppm.

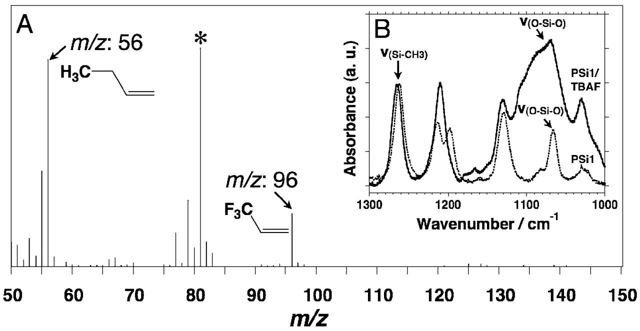
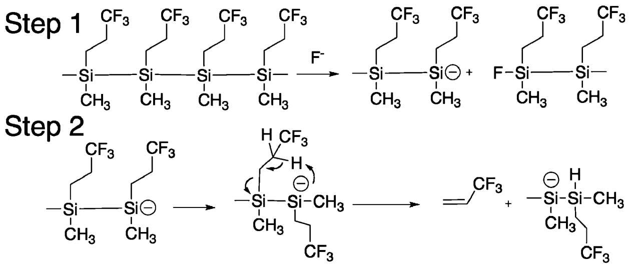


**Figure 3.** (A) GC/MS of gaseous materials generated from **PSi1** upon addition of TBAF. *This peak was not identified. (B) FTIR spectra of **PSi1** before (solid) and 15 min after addition (dotted) of TBAF (KBr method). The peaks were normalized at ca. 1260 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{SiCH3}}$).



**Scheme 1.** Proposed scission mechanism of **PSi3** segment in **PSi1** by $\mathrm{F^-}$.

In conclusion, we demonstrated the facile chemical degelation of polysilane organogel by selective scission of positively charged Si main chains of **PSi3** segments in **PSi1** with TBAF. Although a variety of degradable polymeric materials have been developed,[13] this is the first report on degelable polymer organogelators. Therefore, the present results may lead to potential applications of polymer-based organogels.

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