Novel Molecular Weight and Solvatochromisms in Poly(methyl-3,3,3-trifluoropropylsilane) Induced by Cooperative Through-Space Si···F−C Interactions

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ABSTRACT: Novel helical poly(methyl-3,3,3-trifluoropropylsilane) (**1**) has been synthesized via Wurtz coupling by taking advantage of noncovalent Si···F−C intramolecular interactions. Such weak Si···F−C interactions make the conformation of the polysilane unique and controllable by proper choice of solvent and molecular weight. We have studied the conformation of polysilane by means of UV absorption, photoluminescence, NMR spectra, and viscosity measurements. Polysilane displayed a 7_3 helical rodlike conformation in noncoordinating solvents (e.g., toluene and decane) but a globule-like conformation in coordinating solvents (with N, O, or F as donor) at room temperature. The coordinating nature of solvents played an important role for solvatochromic transition rather than the solvent polarity, as such interactions are competitive in the presence of solvents with donor atoms. On the other hand, an analogous nonfluorinated polysilane, poly(*n*-propylmethylsilane) (**2**), revealed a disordered conformation in coordinating as well as in noncoordinating solvents. The unusual molecular weight dependent UV spectra of **1** showed an isosbestic point, suggesting the equilibrium between globule- and rodlike conformations at room temperature, which was further evident from the viscosity measurements. The proposed weak intramolecular interaction in **1** was supported by the ^{29}Si NMR and ^{19}F NMR in noncoordinating and coordinating solvents. The IR spectrum of cast film from a toluene solution of **1** showed an improper blue shift of 12 cm^{-1} in C−F stretching frequency compared to the IR spectrum cast from THF, suggesting very weak Si···F−C interaction in analogy with blue-shifted hydrogen bonds.

Introduction

Noncovalent interactions, such as hydrogen bonding, metal coordination, and $\pi-\pi$ stacking, are increasingly being utilized to develop well-ordered and self-organized supramolecular materials.[1] Recently, new types of weak interactions, such as C−H···π,[2] C−H···F−C,[3] C−H···O,[4] N···O=C,[5] and X···X (where X is Cl, Br, S, Se),[6] have also been exploited in stabilizing the specific conformations of molecules and molecular assemblies in the solid state. The noncovalent interactions are important in materials comprised of polymer chains, as cooperative effects from a large number of weak interactions can lead to drastic changes in its conformation and properties.[7−14]

The design of a well-defined molecular conformation of synthetic helical polymer has been the subject of considerable recent research interest in the areas of modern polymer science and engineering. Silicon catenated σ-conjugated polysilane is an example of a helical polymer which displays remarkable optical and electronic properties and may serve as a semiconducting quantum silicon molecular wire with 0.2 nm silicon width.[15,16] Such properties of polysilanes strongly depend on global conformation and molecular weight; therefore, control of global conformation and molecular weight contributes to the success of any method for designing helical polymers.

The Wurtz coupling reaction is known to be the most widely used method for the synthesis of high molecular weight alkyl/aryl-substituted polysilanes in appreciable yields.[17] However, this method is of limited potential for functional groups in the polysilanes as the severe polymerization conditions impair the use of functionalized monomers.[17a,18] To our best knowledge, only one report is available on the presence of fluorine atoms in the side chains of polysilane.[19] However, many interesting chemical and physical properties are expected from fluoroalkylated polysilanes similar to fluorinated organic polymers.[20]

In the present study, we have aimed at the synthesis of helical functional polysilanes bearing fluorine atoms in the side chains. We have previously reported that silicon catenated polysilanes adopt rodlike helical architecture induced by specific steric interactions in the presence of only a long alkyl/aryl chain and branching at the β- or γ-position.[21] Recently, we have reported the existence of Si···F−C interactions in fluoroalkylated polysilanes bearing chiral side chains with β- or γ-branching.[22] However, no drastic change in local or global conformation was observed due to such weak interactions with the change in solvent and/or molecular weight.

It is well established that polymers with no chiral centers can also adopt helical conformation with equal population of right- and left-handed screw senses in the presence of sterically bulky substituents.[7] Only few examples of synthetic polymers have been reported recently, wherein the helicity is introduced by hydrogen bonding.[8,11,13] Here we describe a rational design of a rodlike helical poly(methyl-3,3,3-trifluoropropylsilane) (**1**) bearing methyl and trifluoropropyl groups as side chains (Scheme 1), in which the rigidity is induced by subtle manipulation of built in noncovalent Si···F−C

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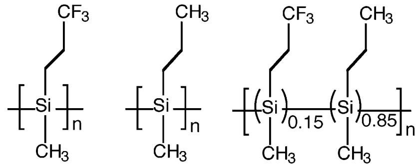
Scheme 1. Chemical Structures of Polysilanes 1−3



1 **2** **3**

intramolecular interactions. The application of weak and reversible Si···F−C interactions lies in controlling the conformation of the polysilane from rod- to globule-like by the proper choice of solvent and molecular weight. Figure 1 shows the schematic presentation of the helical conformation of **1** with equal population of right- and left-handed screw senses in noncoordinating solvents and random coil and/or globule-like conformation in coordinating solvents.

Experimental Section

Measurements. UV and PL spectra were recorded on a JASCO V-570 spectrophotometer and a JASCO FP-6500 spectrofluorometer, respectively. FT-NMR spectra (^{1}H, ^{13}C, ^{29}Si, and ^{19}F) were measured with a JEOL JNM-LA 400 NMR spectrometer. Chemical shifts were referenced to internal tetramethylsilane. Infrared spectra (scan = 32, resolution = 4 cm^{-1}) were obtained on a Horiba FT-730 infrared spectrometer by casting THF or toluene solutions of polysilane on a KBr plate. Molecular weight, polydispersity, and in-line absorption spectra of polysilanes were recorded on a Shimadzu A10 series HPLC apparatus (Polymer Laboratories PL gel 10 μM Mixed B as a column and HPLC-grade THF as eluent at 40 °C) with photodiode array detector. The average molecular weights of polysilanes were measured relative to polystyrene standards. Differential scanning calorimetric (DSC) measurement was carried out using Seiko 6200C DSC instrument with heating rate of 10 °C/min. The intrinsic viscosity−molecular weight relationship was performed using Viscotek T60A detector and RID-10A (Shimadzu Co.) equipped with PLgel Mixed B (Polymer Laboratories Ltd.) at 40 °C using THF as an eluent. The refractive index and the relative viscosity of the eluate were simultaneously recorded with this apparatus. Standard polystyrene of M_w = 116 660 (Viscotek) was used to calculate the apparatus distinctive constant to evaluate the refractive index increment dn/dc of the polymer.

Polymer Preparation. All the reactions were carried out in dried glassware under the dry nitrogen atmosphere using Schlenk techniques. The high molecular weight polysilane (**1**) was synthesized by carefully controlling the reaction conditions, as reported earlier.[19] The polysilane was prepared by dropwise addition of 6.0 g (28.4 mmol) of methyl-3,3,3-trifluoropropyldichlorosilane (Shin-Etsu) to a mixture of 12 mL of dry octane (Aldrich) and 1.3 g (56.5 mmol) of sodium (Wako). The reaction mixture was stirred at 125 °C for 4 h and filtered through a 2.0 μm Teflon filter under nitrogen gas pressure. The crude polysilane was precipitated by careful successive addition of 2-propanol, ethanol, and methanol. The white precipitate was collected by centrifugation and dried overnight at 60 °C in a vacuum. Yield (2.5%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.29 (Si−CH_3, 3H); 1.01 (Si−CH_2, 2H); 2.05 (CH_2CF$_3$, 2H); 3.82 (SiH end group).^{13}C NMR (100.5 MHz, CDCl$_3$): δ −6.2 (br, Si-CH_3); 3.8 (br, Si−CH_2); 30.7 (q, CH_2CF$_3$, $^2J_{C-F}$ = 29.3 Hz); 127.1 (q, CF_3, $^1J_{C-F}$ = 276.2 Hz). ^{19}F NMR (376.1 MHz, THF-d_8): δ −69.9. ^{19}F NMR (376.1 MHz, toluene-d_8): δ −68.2. ^{29}Si NMR (79.4 MHz, THF-d_8): δ −31.4. ^{29}Si NMR (79.4 MHz, toluene-d_8): δ −33.2. IR (cm^{-1}): 2098 (ν_{SiH}); 1265 (δ_{SiMe}); 1211(ν_{C-F}···Si); 1199 (ν_{C-F}); 773 (δ_{C-F}···Si); 749 (δ_{C-F}). The glass transition temperature was −4.1 °C by the DSC measurement.

Polymer **2** was obtained in the following manner. To a mixture of 12 mL of dry toluene (Wako) and 0.9 g (39.8 mmol) of sodium (Wako), 3.0 g (19.1 mmol) of methylpropyldichlorosilane (Shin-Etsu) was added dropwise under a nitrogen atmosphere. The reaction mixture was stirred slowly for 2 h, and the hot reaction mixture was passed through 2.0 μm Teflon filter under nitrogen gas pressure. To the filtrate, ethanol and methanol were added, and the precipitate was collected by centrifugation and dried overnight at 60 °C under vacuum. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.26 (Si−CH_3, 3H); 0.82 (Si−CH_2−CH$_2$−CH$_3$, 2H) 0.98 (CH_3 (Pr), 3H); 1.36 (Si−CH$_2$−CH_2−CH$_3$, 2H).^{13}C NMR (100.5 MHz, CDCl$_3$): δ −4.6 (br, Si−CH_3); 17.8 (br, Si−CH_2−CH$_2$−CH$_3$); 19.1 (br, Si−CH$_2$−CH$_2$−CH_3); 20.5 (br, Si−CH$_2$−CH_2−CH$_3$).^{29}Si NMR (79.4 MHz, CDCl$_3$): δ −32.1.

Copolymer **3** was synthesized similarly as described above. The mixture of (5.0 g, 31.8 mmol) methylpropyldichlorosilane (Shin-Etsu) and (0.45 g, 2.1 mmol) methyl-3,3,3-trifluoropropyldichlorosilane (Shin-Etsu) was added dropwise into 15 mL of dry octane (Aldrich) with 1.7 g (69.0 mmol) of sodium (Wako) at 120 °C, and the solution was stirred for 3 h. The crude polysilane was precipitated by careful successive addition of 2-propanol, ethanol, and methanol. The white precipitate was collected by centrifugation and dried overnight at 60 °C in a vacuum. Yield (15.8%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.24 (Si−CH_3, 6H); 0.81 (Si−CH_2−CH$_2$−CH$_3$, 2H) 0.98 (Si−CH_2−CH$_2$−CF$_3$ + CH_3 (Pr), 5H); 1.36 (Si−CH$_2$−CH_2−CH$_3$, 2H); 2.06 (CH_2CF$_3$, 2H).^{13}C NMR (100.5 MHz, CDCl$_3$): δ −4.4 (br, Si−CH_3); 3.8 (br, Si−CH_2−CH$_2$−CF$_3$); 17.5 (br, Si−CH_2−CH$_2$−CH$_3$); 18.9 (br, Si−CH$_2$−CH$_2$−CH_3); 20.4 (br, Si−CH$_2$−CH_2−CH$_3$); 30.4 (br, CH_2CF$_3$); 126.8 (q, CF_3, $^1J_{C-F}$ = 272.8 Hz). ^{19}F NMR (376.1 MHz, CDCl$_3$): δ −68.5.^{29}Si NMR (79.4 MHz, CDCl$_3$): δ −31.9.

Results and Discussion

The target novel polysilane **1** was synthesized by carefully monitoring the reaction conditions via Wurtz coupling of its corresponding dichlorosilane monomer (CF$_3$CH$_2$CH$_2$SiMeCl$_2$) mediated by molten sodium in octane. IR and multinuclear (^{1}H, ^{13}C, ^{19}F, ^{29}Si) NMR spectra suggest the formation of an idealized structure of polysilane. There was no evidence for the presence of additional signals due to the CF$_2$═CH moiety in ^{1}H and ^{19}F NMR spectra which would have been associated with removal of HF from the side chain in the presence of sodium. This implies that the CF$_2$═CH group is either not present or is too small to be detectable by NMR spectroscopy.

Polysilanes exhibit excitonic UV absorption and photoluminescence (PL) due to σ-conjugation in the silicon backbone.[17] The UV and PL spectra of polysilanes are highly sensitive to changes in helical torsion angle, segmentation, and the regularity of helix. Most of the polysilanes show a broad UV spectrum with narrow PL spectra due to many segments in the silicon backbone with different photoexcitation energies.[17,23] In contrast, rodlike helical polysilanes show mirror images of UV and PL spectra due to a single photoexcitation state.[21]

Figure 2 shows the UV and PL spectra of **1** in toluene at 25 °C. The absorption spectrum revealed a narrow absorption band at 320 nm with a full width at half-maximum height (fwhm) of 8.3 nm. The UV and PL (excited at 315 nm) spectra were mirror images of each other with a very small Stokes shift of 8 nm. The maxima of absorption wavelength (λ_{max}) and fwhm of **1** are consistent with earlier reported 7$_3$ helical (seven silicon atoms in three turns) polysilanes bearing β- and γ- branched side chains, suggesting an adoption of 7$_3$ rodlike helical architecture of **1**.[17a,24] On the other hand, the UV spectrum of an analogous nonfluoroalkylpolysilane, poly(n-propylmethylsilane) (**2**), shows a broad absorption at 305 nm with a fwhm of 35 nm in toluene at room temperature (Scheme 1). The broad UV absorp-

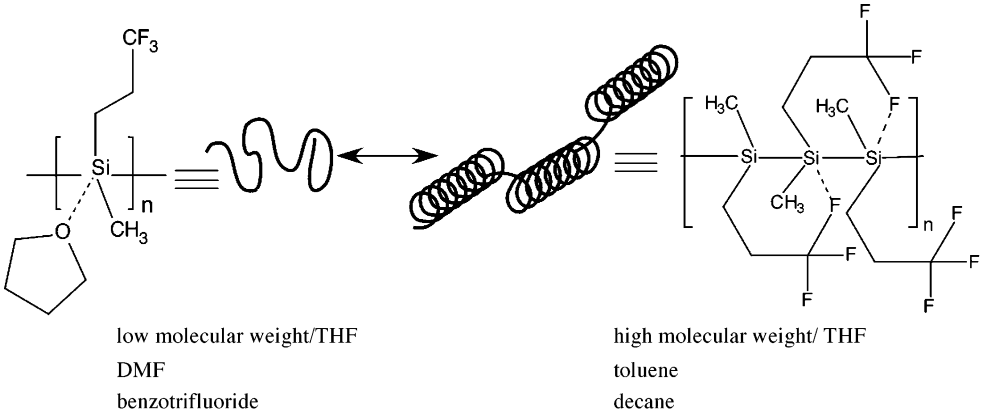


Figure 1. Schematic representations of conformations for **1** in noncoordinating (e.g., decane, toluene) and coordinating solvents (e.g., THF, DMF, benzotrifluoride).

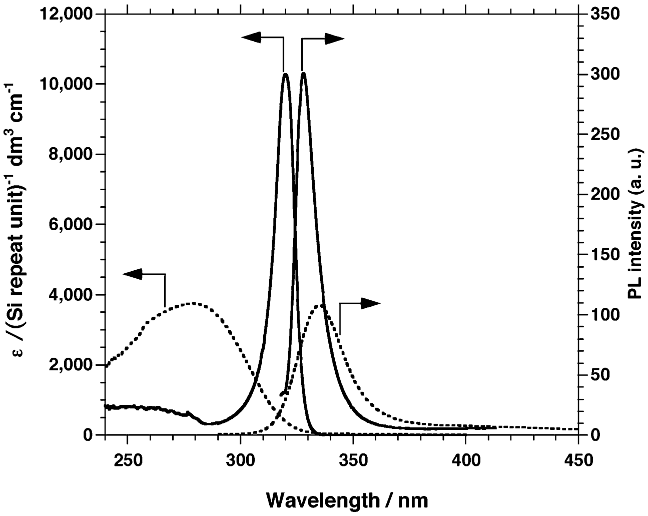


Figure 2. UV and PL spectra of **1** (M_w = 4.1 × 10^5, PDI = 1.5) in toluene (solid line) and DMF (dotted line) at 25 °C.

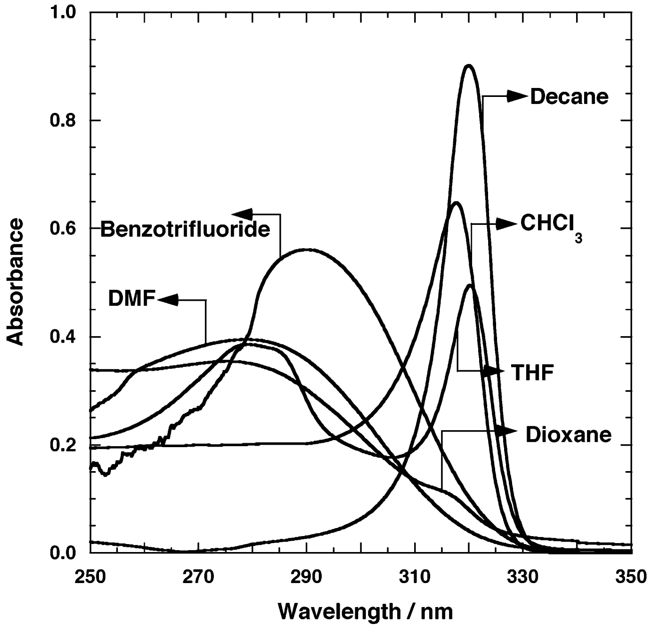


Figure 3. UV spectra of **1** showing solvatochromic transitions in decane, THF, DMF, chloroform, dioxane, and benzotrifluoride at 25 °C.

tion band can be regarded as random coil and/or globule-like conformation of polysilane.[21]

This phenomenon may be the consequence of cooperative weak noncovalent Si···F−C interactions operating between the silicon atoms in the backbone and the fluorine atoms in the side chains. Weak interactions between silicon and fluorine atoms may induce the helicity by providing the steric hinderence and obstructing the segmental motion of the flexible silicon backbone of **1** in toluene.

Similar noncovalent interactions {M···F−C (M = Si, Zr)} are already reported to significantly perturb the conformational equilibrium of small molecules and do not persist in coordinating solvents.[25,26] However, the examples of such weak and reversible interactions are rare in the case of polymers, although they may have potential to control the structure of polymers.[3a,4a,27] Recently, the intramolecular C−H···F−C interactions between the ligand and growing polymer chain have been demonstrated which can manipulate the reactivity of polyolefin catalysts.[3a]

In the present case, the Si···F−C interactions exist between fluorine atoms in the side chains and the *i*th, (*i* + 1)th, or (*i* + 2)th silicon atoms in the backbone to form pseudo five-, six-, or seven-membered rings. We assume that the interactions of fluorine atoms with the neighboring silicon atoms in the backbone may fix into the 7_3 helical conformation of polysilane, while interaction of fluorine atoms with *i*th silicon atoms give the flexible backbone and with (*i* + 2)th silicon atoms may result in a very tight helical conformation. Furthermore, Si···F−C interactions between fluorine atoms and (*i* + 1)th silicon atoms may lead to a sterically favored, more stable six-membered ring.

It is well-known that the strength of such weak noncovalent interaction is very sensitive to solvent.[28] To test this idea in the present study, UV spectra of **1** in different solvents were measured. We observed the remarkable solvatochromism of **1** in noncoordinating and coordinating solvents at room temperature. Although σ-conjugated polysilanes often exhibit thermochromism due to the flexible nature of Si−Si bonds in the backbone, examples of solvatochromism and ionochromism are very rare due to a limited number of available functional polysilanes.[29]

A representative collection of solvent-dependent UV spectra is shown in Figure 3. The spectra revealed blue shifts in λ_{max} of **1** with 3, 28, and 40 nm in chloroform, benzotrifluoride, and dimethylformamide (DMF), respectively, compared to that in toluene and decane.[30] However, the two absorption bands at 280 nm (fwhm = 35 nm) and 320 nm (fwhm = 8.4 nm) were seen in tetrahydrofuran (THF). The PL spectra (excited at 280 nm) of **1** in coordinating solvents (e.g., DMF, benzotrifluoride, etc.) showed a broad emission band at 335 nm with a very large Stokes shift of nearly 50 nm, suggesting globule-like and/or random coil conformation (Figure 2).

It is likely that **1** adopts globule-like conformation in donor solvents and rigid architecture in noncoordinating solvents (e.g., toluene, decane). The main chain rigidity of **1** is further evident from broad ^{29}Si NMR line width (64 Hz) in toluene, suggesting the rigid nature of polysilane backbone. The motion of Si atoms is restricted in the extended rigid architecture, where the narrower line width (20 Hz) in DMF denotes a flexible nature of the polymer.[21]

The UV spectrum of **1** in dioxane (dielectric constant = 2.2) was found to be similar to that in THF (dielectric constant = 7.5), which reveals two absorption bands at 320 and 285 nm. This suggests that the polarity of solvent is not an important factor for solvatochromic transition in this polysilane rather the coordinating nature of solvents contributes to phenomenon of solvatochromism, as such noncovalent Si···F−C interactions are competitive in the presence of solvents with the donor atoms (Figure 1).[25,26]

To further support our idea, we have carried out controlled experiments by using an analogous nonfluoroalkylpolysilane **2** in noncoordinating and coordinating solvents due to the similar size of C−F and C−H groups (Scheme 1). UV, PL, and ^{29}Si NMR spectra of **2** were remained identical in noncoordinating and coordinating solvents. UV spectra of **2** showed a broad band at 305 nm in noncoordinating and coordinating solvents. The fwhm and molar absorptivity (ϵ) of **2** (fwhm = 35 nm; ϵ = 5000 (Si repeat unit)$^{-1}$ dm^3 cm^{-1}) were found to be similar to those of **1** in coordinating solvents (fwhm = 35 nm; ϵ = 3800−4700 (Si repeat unit)$^{-1}$ dm^3 cm^{-1}). These results clearly suggested that **1** (in coordinating solvents; without Si···F−C interactions) and **2** (in noncoordinating and coordinating solvents) adopt random coil and/or globule-like conformation,[21] which is an agreement with our proposed hypothesis.

The origin of two absorption bands in THF is surprising and assumed to originate from two different global/local conformations: the narrow 320 nm absorption is attributed to the “locked” rigid helical conformation of **1** due to Si···F−C backbone−side chain interaction, and the broad 280 nm band is due to “unlocked” globule-like conformation, in which no interaction is present between the side chain and polymer backbone. This is much clearer from the change in UV absorption spectra of **1** with different molecular weights in THF.

Figure 4 shows the increase in intensity of the narrow 320 nm band with increase in molecular weight of **1**. A fully formed rodlike architecture was realized with high molecular weight ($M_w = 3.4 \times 10^5$; PDI = 3.3) due to cooperative effect of Si···F−C interactions, whereas the UV spectrum of low molecular weight ($M_w = 2.0 \times 10^4$, PDI = 1.3) showed only the broad 285 nm band in THF, signifying the dominant conformation to be globule-like.[19]

Rigid wormlike polymers generally adopt rodlike architecture in the low molecular weight range, while attaining a random coil conformation in the high molecular weight range. As an exception to this general rule, the polymer with rigid building blocks may adopt a globule-like conformation with a low degree of polymerization and a rodlike conformation with a high degree of polymerization.[1c] The unusual effect of molecular weight dependency on the observed absorption spectrum of **1** showed a clear isosbestic point, suggesting the equilibrium between globule- and rodlike architecture of polysilane.

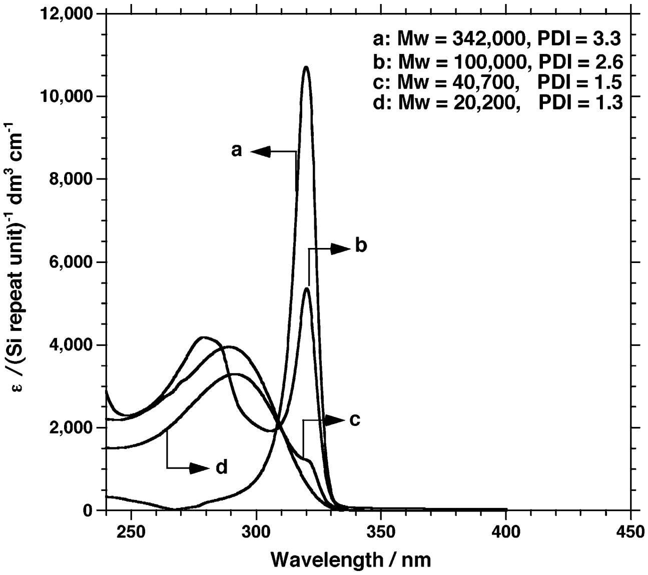


Figure 4. Change in the UV absorption spectra of **1** with molecular weight in THF at 25 °C.

Many biological and synthetic polymers exhibit conformational transitions between ordered (e.g., helix, rod) and disordered states (e.g., coil, globule) by external stimuli such as temperature, solvent, molecular weight, pH, and light.[31] Polysilanes exhibit only thermochromic behavior depending on the nature of substituents due to limited availability of polysilane bearing polar groups.[17] Although well-ordered thermodriven conformational transitions between two ordered states (e.g., all-trans-helix, helix−helix) and order to disorder states have been demonstrated theoretically and experimentally,[32] the present fluoroalkylated polysilane (**1**) may be the first example in which the silicon catenated polymer undergoes the molecular weight-dependent conformational change.

The population of rod- and globule-like conformation of **1** in THF was evaluated by the relative intensity of absorption bands at 320 and 285 nm, which are due to rod- and globule-like conformation, respectively. This allowed us to estimate the equilibrium constant (K) between two transition states of **1** in THF at particular temperature, which was used to estimate free energy of transition ($\Delta G° = -RT \ln K$).

$$\text{globule} \rightleftharpoons \text{rod}$$

Figure 5 shows the plot of free energy ($\Delta G°$) as a function of absolute temperature (T). The intercept of the plot gives the value of enthalpy (2.65 kJ/mol). The magnitude of Si···F−C noncovalent interactions per Si repeating unit was estimated by dividing the enthalpy with degree of polymerization, evaluated on the basis of weight-average molecular weight ($M_w = 1.0 \times 10^5$, PDI = 2.6). The magnitude of weak Si···F−C interaction in THF was then estimated to be only 3.76 J/Si repeating unit. The cooperative and amplified behavior of such noncovalent intramolecular interactions of **1** may lead to its stiff architecture.

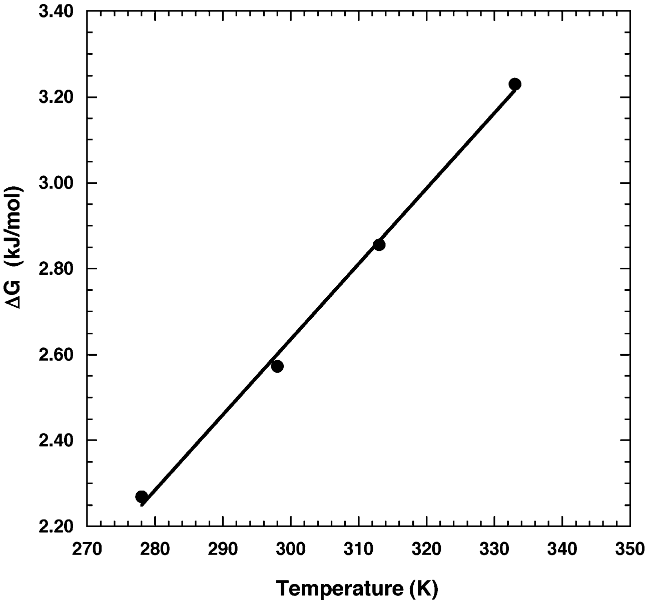


Figure 5. Plot of free energy ($\Delta G°$) of **1** ($M_w = 1.0 \times 10^5$, PDI = 2.6) as a function of temperature in THF solution.

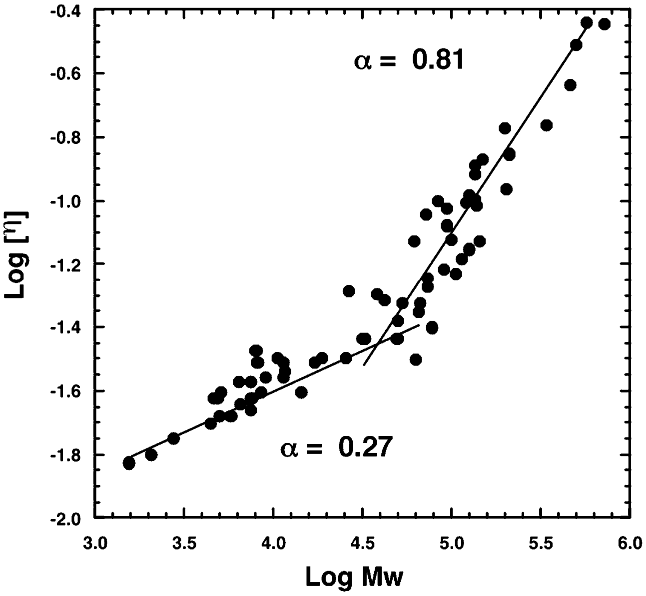


Figure 6. Mark−Hauwink−Sakurada plots of **1** over a wide range of molecular weights (1.58×10^3−6.30×10^5).

The unusual molecular weight-dependent change in global conformation of **1** was also evident by the viscosity measurement. The viscosity index, α, indicates the contraction and expansion of polysilane chains in solution, obtained from the Mark−Houwink−Sakurada plot, $[\eta] = K[M]^\alpha$, where K, η, and M are constant, intrinsic viscosity, and molecular weight, respectively. Figure 6 shows the plots for four different samples of **1**, which cover wide range of molecular weight (1.6×10^3−6.3×10^5). The slope (α) of the plots ($\log[\eta]/\log M_w$) was evaluated to be 0.27 in the lower molecular weight region ($1.6 \times 10^3 < M_w < 4.0 \times 10^4$), suggesting almost globule conformation of **1**, while α was 0.81 in the high molecular weight region ($4.0 \times 10^4 < M_w < 6.30 \times 10^5$), indicating rigid polymer to the contrary.[21] This clear bend from the slope is absolutely consistent with the observed effect of the molecular weight-dependent UV spectra, which further suggests the rod−globule-like transition as a function of molecular weight.

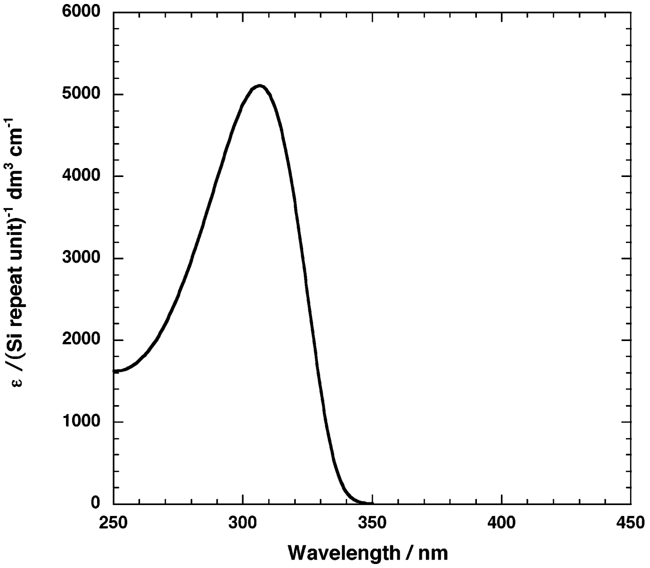


Figure 7. UV spectrum of **3** ($M_w = 3.1 \times 10^5$, PDI = 1.5) in octane at 25 °C.

Figure 6 also depicts a critical molecular weight in THF above which **1** adopted a stiff architecture. It is noteworthy that critical molecular weight (41 600) was comparable with that obtained from molecular weight-dependent UV spectra in THF, as shown in Figure 4c. This critical molecular weight in THF suggested that approximately 300 silicon atoms are required for conformational change. The energy barrier for rod−globule transition was estimated to be 1.13 kJ/mol by the product of magnitude of weak Si···F−C interaction per silicon repeat unit and the number of silicon atoms involved in Si···F−C cooperativity in THF. It was expected that the magnitude of the Si···F−C interaction was at least 4 times more in noncoordinating solvent (toluene or decane) than the coordinating solvent (THF) as only a narrow absorption band at 320 nm was observed in toluene with molecular weight ($M_w = 1.1 \times 10^4$, PDI = 1.1) 4 times less than the critical molecular weight in THF.

For comparison, the UV spectrum of copolymer **3** was recorded (Scheme 1). Figure 7 showed a broad absorption only at 305 nm with fwhm of 35 nm, suggesting the globule-like conformation of **3**. In this case, the shape of UV spectra remained unchanged with different molecular weights and solvents. We believe that *n*-propyl groups of **3** act as defects of Si···F−C cooperativity, and thus no change in conformation was observed even with sufficiently high molecular weight sample ($M_w = 3.1 \times 10^5$, PDI = 1.5) of **3** in noncoordinating and coordinating solvents.

The existence of Si···F−C interaction in THF as mentioned above may be interpreted by IR spectra of **1** ($M_w = 1.0 \times 10^5$, PDI = 2.6) in the solid film. The IR spectrum of cast film from THF solution is highly informative, which revealed two symmetric C−F stretching bands at 1199 and 1211 cm^{-1}, respectively, as shown in Figure 8a.[33] The 1211 cm^{-1} band may be due to the formation of pseudo five-, six-, or seven-membered ring arising from intramolecular and/or intermolecular Si···F−C interaction operating between side chain and backbone and the former band (1199 cm^{-1}) from linear side chain having no interaction between main chain and side chain, as shown in Figure 2b. This is evident from the IR spectrum of polysilane casting from toluene

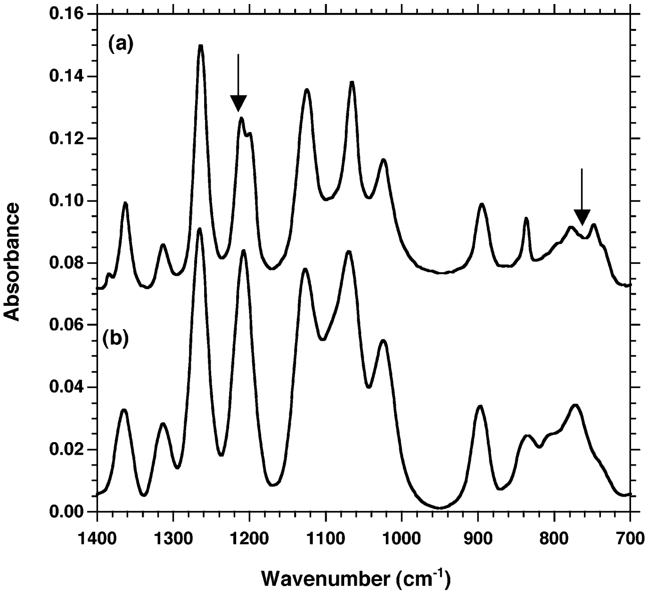


Figure 8. IR spectrum of **1** (M_w = 1.0 × 10^5, PDI = 2.6): (a) cast from THF solution; (b) cast from toluene solution.

solution. The spectrum showed only the 1211 cm^{-1} band with increase in intensity, while the band at 1199 cm^{-1} completely disappeared (Figure 8b). Similar spectral characteristics were observed for the δ_{C-F} vibration in the film cast from toluene solution with a shift of 24 cm^{-1} toward higher frequency in comparison to casting from THF solution (749 cm^{-1}).

The blue shift in the ν_{C-F} band is quite surprising and may be explained with an analogy of improper, blue-shifted hydrogen bond. The theoretical studies showed that weak X−H···Y hydrogen bond formation gives rise to unexpected blue shift in the X−H stretching frequency, resulting into the shortening of X−H bond.[34] This phenomenon is applicable only for weak hydrogen bonds in which rehybridization factor (responsible for shortening of X−H bond) is more pronounced than hyperconjugation that causes lengthening of X−H bond. Recently, a few experimental evidences of blue-shifted hydrogen bonds were reported in matrix isolation and at low temperature.[34a,e] The blue shift of the ν_{C-F} band in the IR spectrum of **1** was in good agreement with earlier reports on blue-shifted hydrogen bonds. This blue shift was ascribed to weak Si···F−C interactions and provided the first experimental evidence for blue-shifted weak interaction in the solid film at room temperature.

The existence of coordinative Si···F−C interactions was also demonstrated by ^{19}F and ^{29}Si NMR spectroscopy. Figure 9 showed a comparison of the ^{29}Si NMR spectrum of **1** in toluene-d_8 and THF-d_8. The spectrum revealed broad resonances centered at δ −33.2 in toluene due to the silicon catenated polymer backbone. The ^{29}Si NMR spectrum showed a downfield chemical shift of 1.8 ppm in THF-d_8 compared to that in toluene-d_8. The concomitant upfield shift of 1.7 ppm was found in the ^{19}F NMR spectra in THF-d_8 (δ −68.2) with respect to toluene-d_8, as shown in Figure 10. These small changes in the chemical shifts suggested a very weak interaction between Si and F atoms and are consistent with only recent reports in which noncovalent Si···F interaction was proposed in molecular system by means of NMR and X-ray crystal structure analyses.[25,35]

The proposed through-space Si···F−C interaction was supported by difference in NOE ^{19}F NMR spectra in toluene. A clear NOE attenuation was observed in ^{19}F NMR spectrum upon irradiation of ^{29}Si resonance at δ −33.2. Also, weak coordinative interaction in **1** was evident by the presence of a doublet at δ −68.2 (J_{Si-F} = 32.4 Hz) in the ^{19}F NMR spectrum in toluene-d_8, which was found to be absent in THF-d_8.

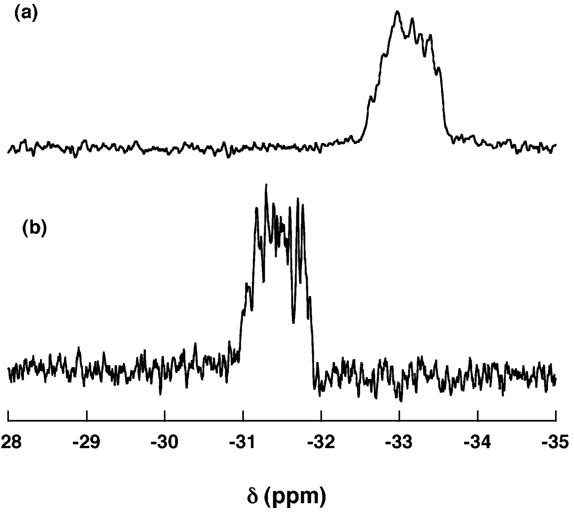


Figure 9. $^{29}Si\{^1H\}$ NMR spectrum of **1** (M_w = 1.1 × 10^4, PDI = 1.1) at 25 °C (a) in toluene-d_8 and (b) in THF-d_8.

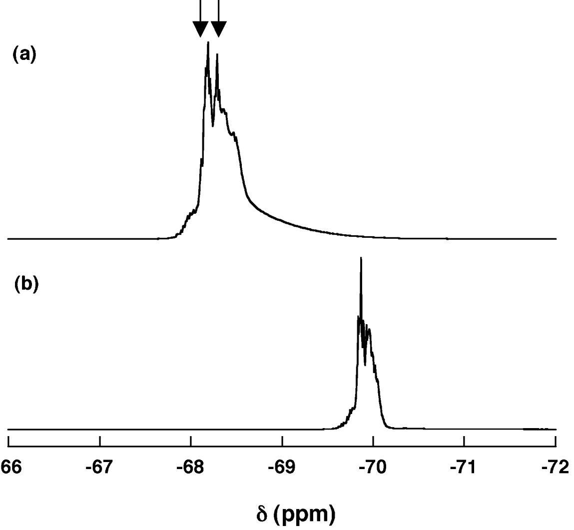


Figure 10. $^{19}F\{^1H\}$ NMR spectrum of **1** (M_w = 1.1 × 10^4, PDI = 1.1) at 25 °C (a) in toluene-d_8 and (b) in THF-d_8.

Conclusions

We demonstrated the clear spectroscopic evidences for through-space Si···F−C interaction in poly(methyl-3,3,3-trifluoropropylsilane) at room temperature. ^{29}Si NMR, ^{19}F NMR, and IR spectra in noncoordinating and coordinating solvents supported the proposed Si···F−C interaction in **1** at room temperature. Weak Si···F−C interaction resulted in lengthening of C−F bonds as evident from the 12 cm^{-1} blue shift in the ν_{C-F} band in the IR spectrum with an analogy of improper, blue-shifted hydrogen bonds. This work highlights the potential of cooperative and weak Si···F−C interactions in controlling desired conformation of **1** by the choice of solvent and molecular weight. The contribution of such intramolecular interactions to fix into the helical conformation was supported by variation in UV, PL, and NMR (^{29}Si and ^{19}F) spectra of **1** in coordinating solvents and by comparing the UV spectrum of **1** with an analogous nonfluoroalkylpolysilane, poly(*n*-propylmethylsilane). This is the first report of molecular weight-dependent conformational change of polysilane. The exceptional molecular weight-dependent UV spectra suggested rod- to globule-like transition, which was further evident by the value of viscosity index (α) evaluated from the Mark−Houwink−Sakurada plot. This weak Si···F−C interaction may potentially be exploited for the strategic design of new molecular, supramolecular, and polymeric architectures.

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