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Preparation and Characterization of a Novel Organopolysilane. (3,3,3-Trifluoropropyl)methylpolysilane

Masaie Fujino,* Tomoko Hisaki, Michiya Fujiki, and Nobuo Matsumoto

NTT Basic Research Laboratories, Musashino, Tokyo 180, Japan

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ABSTRACT: The first soluble (fluoroalkyl)polysilane high polymer was prepared by a conventional Wurtz-type reaction of dichlorosilane and sodium in *n*-paraffins above 150 °C. The structure of this polymer was determined by elemental analyses (C and H), gel permeation chromatography, and spectral analyses [FT-IR, FT-NMR (^1H, ^{13}C, ^{19}F, and ^{29}Si), and UV]. The molecular weight distribution of the polymer was monomodal, and the weight-average molecular weight of this polymer was 31 000. The UV absorption maximum due to Si catenation was at 285 nm. This is the shortest wavelength yet reported for an organopolysilane high polymer. The thermochromic behavior of this polymer was also observed in the solid state at temperatures from −120 to +100 °C. The polymer began to decompose at around 200 °C, and its glass transition temperature was −3 °C, which was higher than that of the nonfluorinated polymer.

Introduction

Organopolysilanes,[1] a new class of σ-conjugated inorganic polymers, have received much attention because of their various physical properties. They exhibit conductivity,[2] photoconductivity,[3] nonlinear optical susceptibility,[4] and other optical properties.[5] Although these physical properties could be adjusted by varying the functional side chains, synthetic procedures have restricted most investigations to organopolysilanes containing only alkyl and aryl substituents.[1] Because most organopolysilanes have been obtained by a Wurtz-type reaction of dichlorosilanes and sodium metal, one might believe that they can only be synthesized with side chains that do not react with molten sodium. In fact, there have been no reports on the synthesis of well-defined organopolysilane high polymers with nonalkyl or nonaryl side chains.

We will focus here on a fluoroalkylated organopolysilane. Interesting chemical and physical properties can be expected from this polymer because carbon-backbone polymers containing fluorine often exhibit ferroelectricity and pyroelectricity, as well as water and oil repellency.[6] When synthesizing this polysilane, reaction between the fluorinated side groups and sodium should be prevented. Although the C–F bond seems to be less reactive to sodium than are C–Cl, C–Br, and C–I bonds, fluorinated organic compounds in general could react violently with sodium.[7] A preliminary study revealed that a fluoroalkylpolysilane high polymer could nonetheless be prepared by using the Wurtz-type reaction.[8] This paper describes the synthesis and characterization of the first soluble fluoroalkylpolysilane high polymer, (3,3,3-trifluoropropyl)methylpolysilane (1), which was obtained by controlling the reaction temperature.

$$-[CF_3CH_2CH_2(CH_3)Si]_n-$$

1

Results and Discussion

Preparation. Polymerization was carried out by using the conventional Wurtz-type reaction:

$$CF_3CH_2CH_2(CH_3)SiCl_2 \xrightarrow[150-200\ °C]{Na} 1$$

The essence of our procedure is that the (3,3,3-trifluoropropyl)methyldichlorosilane monomers are polymerized above 150 °C in hydrocarbon solvents.

This polymerization was sensitive to the reaction temperature. Polymer 1 was formed only above 150 °C, and only low molecular weight compounds were produced when the reaction was carried out below 150 °C (Table I). (One of the major low molecular weight compounds was the cyclic pentamer $[CF_3CH_2CH_2(CH_3)Si]_5$.[25]) There is no temperature threshold for polymerization of nonfluorinated alkyl- or arylpolysilanes: ordinary organopolysilanes are generally formed using toluene at temperatures around 110 °C, and the yields of those polymers increase monotonically as the polymerization temperature increases in a series of *n*-alkane solvents.[9] The yield of 1 was highest when the polymerization was carried out between 153 and 165 °C in *n*-decane. In contrast, no polymer was obtained when using toluene or even the polar solvent systems 7:3 toluene/diglyme and 7:3 decane/diglyme from which ordinary organopolysilanes are obtained with higher yields.[10] Neither lithium nor magnesium metals in tetrahydrofuran (THF) yielded polymer 1, nor did Na/K alloy in toluene. The use of a crown ether (18-crown-6), which is known to increase the yield of alkylpolysilanes and improve the distribution of their molecular weights,[12] yielded an unknown polymer instead of polymer 1.[13] These facts indicate that the formation of 1 is more sensitive to the polymerization temperature than to the solvent polarity.

The formation of 1 might be thermodynamically controlled, with cyclization predominating below a characteristic temperature and extension of the high polymer 1 additionally proceeding above that temperature. A higher polymerization temperature would promote thermal decomposition, decreasing the yield of the polymer. Thermal decomposition of 1 at around 200 °C, revealed by TG analysis, will be described later in this paper.

Elemental analyses for C and H agree with the values calculated for the desired structure 1.[14] The molecular weight distribution of polymer 1 (Figure 1) was monomodal, and the weight-average molecular weight of this polymer (M_w) was 31 000 (M_w/M_n = 2.1).

The IR absorption spectrum of polymer 1 (Figure 2) indicates the presence of methyl and 3,3,3-trifluoropropyl groups.[15] There is no evidence for siloxane moieties because the spectrum does not show their characteristic broad absorption (due to Si–O–Si bonding) between 1000 and 1110 cm^{-1}. Two weak peaks absent from the spectrum of the monomer are seen at 1856 cm^{-1} and at about 2100 cm^{-1}. The shorter wavelength peak can be assigned to the

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Table I
Yields of (3,3,3-Trifluoropropyl)methylpolysilane

run	solvent	bp of solvent, °C	temp, °C	time, h	yield,[d] %
1[a]	toluene	111	reflux	1	none
2[a]	7:3 toluene/ diglyme[c]		reflux	1	none
3[b]	dodecane	215	131–137	5	none
4[b]	7:3 decane/ diglyme[c]		146–149 (reflux)	5	none
5[b]	decane	174	153–165 (reflux)	5	4
6[b]	undecane	195	165–178 (reflux)	5	3
7[b]	dodecane	215	170–191 (reflux)	5	1.5

[a] Solvent, 50 mL; monomer, 0.0237 mol; Na, 2.4 × (the number of moles of monomer). [b] Solvent, 100 mL; monomer, 0.0948 mol; Na, 1.2 × (the number of moles of monomer). [c] Volume ratio. [d] Moles of polymer per moles of monomers.

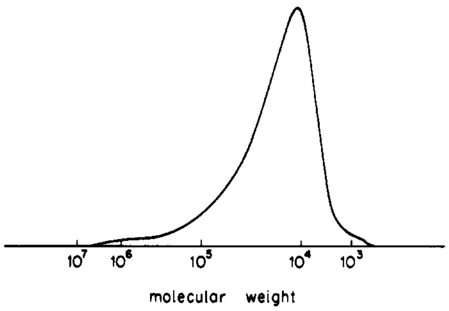

Figure 1. Molecular weight distribution of (3,3,3-trifluoropropyl)methylpolysilane.

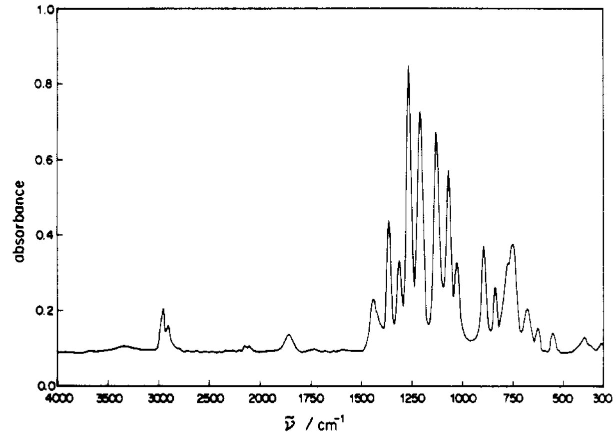

Figure 2. FT-IR spectrum of a (3,3,3-trifluoropropyl)methylpolysilane film on KBr.

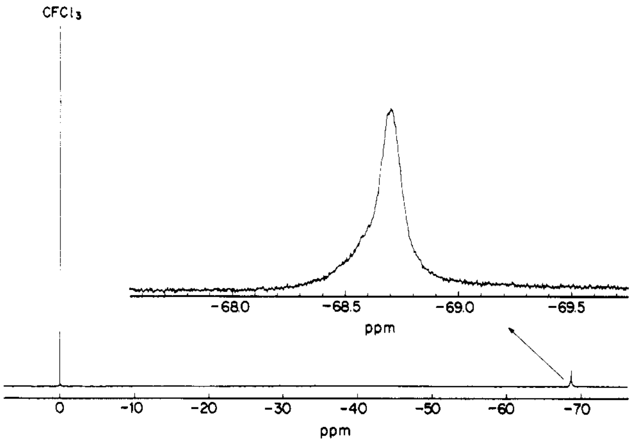

Figure 3. ^{19}F FT-NMR spectrum of (3,3,3-trifluoropropyl)methylpolysilane (in $CDCl_3$ at room temperature, 376.29 MHz, $CFCl_3$).

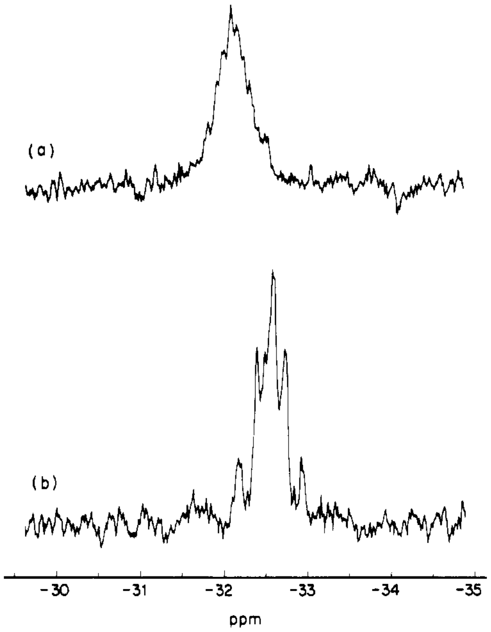

Figure 4. ^{29}Si FT-NMR spectra of (a) (3,3,3-trifluoropropyl)methylpolysilane and (b) MPrPSi (each in THF-d_8 at room temperature, 80 MHz, $(CH_3)_4Si$).

$CH{=}CF_2$ moiety—derived from the side reaction between sodium and the 3,3,3-trifluoropropyl group, followed by elimination of HF. The 2100-cm^{-1} peak can be attributed to Si–H groups, which suggests that a silyl radical may be an intermediate during the polymerization. This silyl radical would be formed by the reaction between sodium and the silyl chloride monomer. This reaction would transfer one electron and would subtract hydrogen from the solvent or an α-hydrogen from the 3,3,3-trifluoropropyl group. Although the IR spectrum of polymer 1 indicated small amounts of these polar moieties, they were not detected in the ^1H, ^{13}C, or ^{29}Si NMR spectra.

The three proton peaks in the ^1H NMR spectrum of polymer 1 were at 0.47 ppm (br, $SiCH_3$, 3 H), 1.12 ppm (br, $SiCH_2$, 2 H), and 2.20 ppm (br, CH_2CF_3, 2 H). The four carbon peaks in the ^{13}C NMR spectrum were at −6.7 ppm (br, $SiCH_3$), 4.4 pm (br, $SiCH_2$), 29.46 ppm (t, CH_2-CF_3, $J_{C2\text{-}F}$ = 30.2 Hz), and 126.57 ppm (q, CF_3, $J_{C3\text{-}F}$ = 277.3 Hz). The ^{19}F NMR spectrum of polymer 1 dissolved in $CDCl_3$ (reference: $CFCl_3$) showed a broad peak from the CF_3 group at around −68.7 ppm (see Figure 3), whereas the peak due to the CF_3 group of the monomer was at −68.319 ppm (t, $J_{F\text{-}H}$ = 10.536 Hz). This is similar to the fluorine chemical shifts for other alkanes that include the trifluoromethyl group; these shifts are usually seen around −60 to −70 ppm.[16]

Figure 4 shows the ^{29}Si NMR spectra of polymer 1 and its parent, nonfluorinated, methylpropylpolysilane (MPrPSi) in THF-d_8. Polymer 1 gives a broad resonance peak at −32.1 ppm, and there are no other peaks between +20 and −180 ppm. This indicates that there are no branches in its Si backbone. The chemical shift of Si in the fluorinated monomer shows a weak electron-withdrawing effect because it is 1.358 ppm downfield from that of the monomer of the parent MPrPSi ($CH_3CH_2CH_2(CH_3)$-$SiCl_2$).[18] The chemical shift of Si in polymer 1, on the other hand, is shifted only about 0.4 ppm downfield from that of MPrPSi.[19] This rather small difference in the chemical shift of Si between polymer 1 and MPrPSi might be attributed to the difference in the conformational structure of the Si backbone for the two polymers. In fact, the chemical shift of Si in dihexylpolysilane is shifted about 3 ppm upfield when its conformation changes from

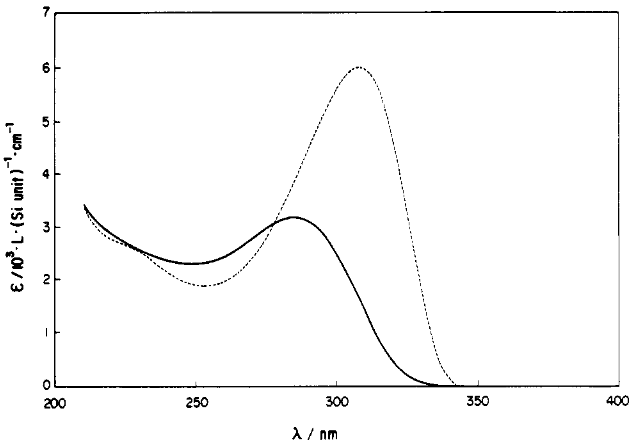

Figure 5. UV absorption spectra of organopolysilanes dissolved in THF (solid curve, 3,3,3-trifluoropropyl)methylpolysilane, M_w = 31 000, 4.0 × 10^{-4} (Si unit·mol)/L; dashed curve, MPrPSi, M_w = 90 000, 1.6 × 10^{-4} (Si unit·mol)/L).

an all-trans structure to a random-coil structure. It thus appears that the chemical shift of Si in polymer 1, relative to Si in MPrPSi, results from the electron-withdrawing effect of three fluorines in the γ position (downfield effect) and from the intensely helical structure (upfield effect).

All the ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectral assignments of polymer 1, based on those of its monomer, are thus consistent with the desired linear polymer 1 having both methyl and 3,3,3-trifluoropropyl side chains.[18,21] Successful preparation of polymer 1 without significant decomposition of the fluoroalkyl group demonstrates the possibility of developing organopolysilanes with a variety of functions. The optoelectrical property of this polymer will be presented elsewhere.

UV Absorption. Figure 5 shows the UV absorption spectra of polymer 1 and MPrPSi dissolved in THF. The absorption maximum (λ_{max}) was observed at 285 nm, providing evidence of linear catenation of silicon atoms. No characteristic vibrational structures were indicated. The λ_{max} of this polymer was blue-shifted 23 nm from that of MPrPSi. As far as we know, this is the shortest λ_{max} seen for any high molecular weight organopolysilane. When the M_w of an organopolysilane is more than about 10 000, the characteristic λ_{max} due to the Si backbone is usually independent of molecular weight. In a series of permethyloligosilanes [Me(SiMe$_2$)$_n$Me, where n indicates the degree of oligomerization], the λ_{max} of the oligomer tends to saturate when n is greater than 10.[1a] Furthermore, the λ_{max} of the low molecular weight MPrPSi (M_w = 20 000) was the same as that of the higher molecular weight polymer (M_w = 90 000). The blue shift in polymer 1 was therefore independent of the degree of Si catenation. The blue shift is also unlikely to be caused by the inductive effect of the fluorine in the 3,3,3-trifluoropropyl group because, as shown by the ^{29}Si NMR analysis, fluorine's electron-withdrawing effect on Si is quite small.

The λ_{max} of polysilanes is, however, very sensitive to the conformation of the Si backbone. A large blue shift of about 50 nm in the UV absorption spectrum of dihexylpolysilane, showing thermochromism, was due to the change from all-trans to random-coil structures.[11] Theoretical studies also predict that the UV absorption peak due to electronic transition between valence and conduction bands in the Si backbone[22] will be greatly blue-shifted as the helical angle of the Si backbone varies from 180° (all-trans) to 80° (helix).[23] Because polymer 1 has the bulky 3,3,3-trifluoropropyl group instead of the propyl group, it can assume a conformational structure with a helical angle smaller than that of MPrPSi. Such a helical structure will produce a larger blue shift. The introduction of fluorine at a position far from the main chain is likely to transform the conformation of a polymer. In fact, the 1/3 helix structure of isotactic polystyrene changes into a 1/4 helix structure when the para hydrogen of the phenyl ring is replaced with fluorine.[24]

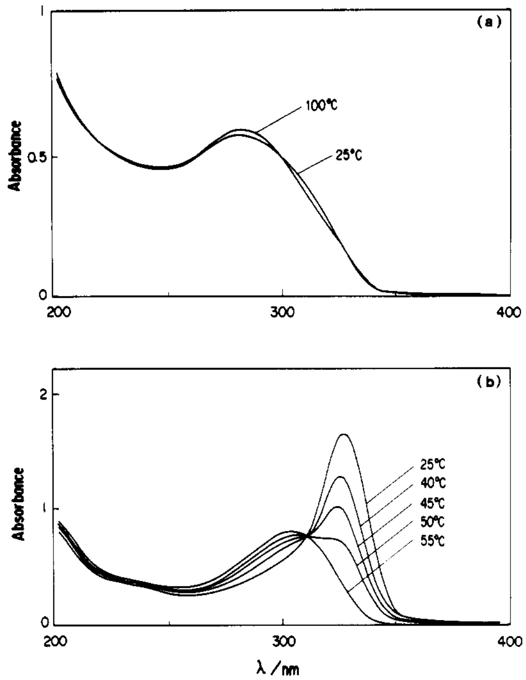

Figure 6. Temperature dependence of UV absorption spectra of the solid films of (a) (3,3,3-trifluoropropyl)methylpolysilane and (b) MPrPSi.

Thermochromism in the Solid State. Like other organopolysilanes, polymer 1 exhibited reversible thermochromism at wavelengths in the UV region. Figure 6 shows the temperature dependence of polymer 1's UV absorption in the solid state. A small change is seen in the UV absorption spectrum, along with slight red shift of the λ_{max}. These differ from the larger spectrum changes of the parent MPrPSi, whose λ_{max} is blue-shifted by 24 nm at temperatures from 25 to 55 °C. The essential difference between polymer 1 and MPrPSi is whether or not the melting of microcrystals formed in the polymer is associated with the thermochromic behavior. With polymer 1, no exothermic peaks due to melting were observed between −190 and +150 °C in DSC. This polymer's X-ray diffraction pattern did not show peaks indicating microcrystals. This indicates that melting was not associated with the thermochromic behavior of polymer 1; therefore the spectrum change is due to changes occurring in the amorphous phase. The thermochromism of MPrPSi, on the other hand, is due to the melting of its microcrystals. As shown in Figure 6, the spectrum change of MPrPSi takes place above the melting point (40 °C).

The thermochromic behavior of polymer 1 can be understood in detail by considering the second derivative of the original UV absorption spectrum. Valleys in the second-derivative spectrum (Figure 7) at 285 and 314 nm respectively correspond to the λ_{max} and shoulder absorption in the original spectrum. The shoulder absorption was only seen when the polymer was in the solid state; it was not observed when the polymer was in solution. There were two characteristic features of this second-derivative spectrum. First, the red shift of the λ_{max} was seen in a temperature range that is relatively low compared with other organopolysilanes in the solid state. The λ_{max} was

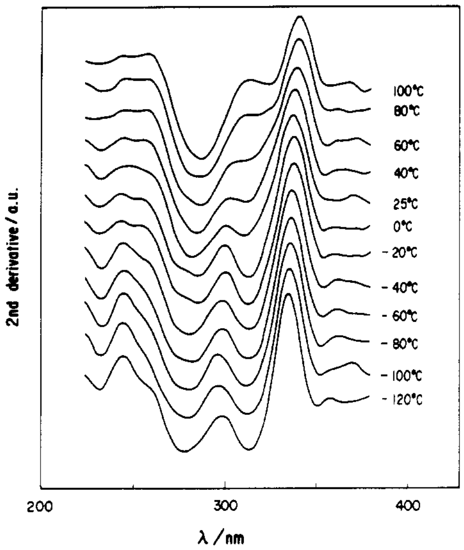

Figure 7. Second derivatives of UV absorption spectra of (3,3,3-trifluoropropyl)methylpolysilane at various temperatures.

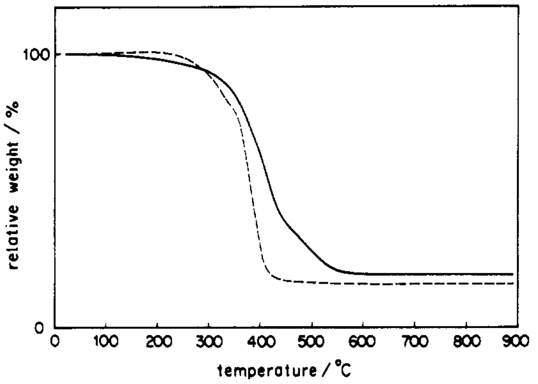

Figure 8. TG profiles of (3,3,3-trifluoropropyl)methylpolysilane (solid curve) and MPrPSi (dashed curve) in a stream of nitrogen. Heating rate: 10 °C/min.

278 nm at −120 °C and shifted gradually toward red when temperature increased: it was 285 nm at room temperature and 289 nm at 100 °C. Second, the shoulder absorption at 314 nm began to disappear above 0 °C, in connection with the glass transition of polymer 1. As described below, the glass transition temperature (T_g) was −3 °C. Because the thermochromic behavior was reversible, it could not have been caused by thermal decomposition. The thermochromic behavior of the shoulder absorption is therefore strongly related to the segmental motion. That is, this absorption appears when the segmental motion is frozen. A small amount of a conformation different from the intense helix in polymer 1 would be formed in the solid state. Interaction between side chains with different Si backbones, which is important for organopolysilanes in the solid state, could induce the new conformation.

Thermal Properties. Thermal properties were also affected by the introduction of the fluorinated alkyl chain. Figure 8 shows the TG profile of polymer 1 in a stream of nitrogen. This polymer began to decompose at around 200 °C, losing 5% of its weight at 282 °C and 10% at 329 °C. Only a 20% residue remained at 560 °C. The parent MPrPSi was stable up to about 250 °C and then lost weight more rapidly than did polymer 1. The excess stress energy due to the bulkiness of the fluorinated alkyl side chain could be the reason that polymer 1 began to decompose at a lower temperature. Because most organopolysilanes are converted to silicon carbide (SiC),[1a] the residue at 560 °C was probably SiC. The amount of the residue from polymer 1 was nearly as small as the residue from MPrPSi (15%) but was much closer to the amount of SiC that would remain if silicon were not lost in volatile products (28.6% conversion to SiC for polymer 1 vs 46.5% for MPrPSi). It therefore appears that fluorination of side chains in organopolysilanes would facilitate their effective transformation to SiC ceramics.

The T_g of polymer 1 was evaluated by DSC to be −3 °C, whereas the T_g of MPrPSi was −28 °C. Fluorination of the alkyl side chain thus increased the T_g of this polymer by 25 °C. Substituting the bulky 3,3,3-trifluoropropyl group for a propyl group must increase the energy barrier to rotation around the Si backbone, and this increases T_g. The higher polarity of the 3,3,3-trifluoropropyl group, which may also increase the interchain cohesive energy, may also contribute to the higher T_g of polymer 1.

Conclusion

The first soluble fluoroalkylpolysilane high polymer, (3,3,3-trifluoropropyl)methylpolysilane, was prepared by a conventional Wurtz-type reaction of dichlorosilane and sodium in a restricted temperature range. This polymer was characterized by elemental analyses (C and H), GPC, spectral analyses [FT-IR, FT-NMR (^{1}H, ^{13}C, ^{19}F, and ^{29}Si), and UV], and thermal analyses (TG and DSC). The molecular weight distribution of the polymer was monomodal, and the weight-average molecular weight was 31 000. When the polymer was dissolved in THF, the absorption maximum due to Si catenation was at 285 nm. This is the shortest wavelength ever reported for an organopolysilane high polymer. When a solid film of the polymer was warmed from −120 to +100 °C, its λ_{max} (278 nm at −120 °C) exhibited a red shift, and, associated with the polymer's glass transition, the shoulder absorption at 314 nm disappeared above 0 °C. The T_g of this polymer was −3 °C, which is 25 °C higher than the T_g of MPrPSi. This polymer began to decompose when heated to about 200 °C, and it left a residue containing an amount of SiC that was closer to the ideal than was the amount of residue left from MPrPSi. This suggests that fluorination of the alkyl side chains in organopolysilanes makes their transformation to SiC more efficient.

The preparation of organopolysilane copolymers with fluoropropyl side chains will be described in a forthcoming paper.

Experimental Section

Preparation of Polymer 1. Freshly distilled monomer (20 g; Shin-Etsu Chemical) was added dropwise to 2.6 g of sodium metal suspended in 100 mL of refluxing dry decane vigorously stirred under an argon atmosphere. After 5 h, the reaction mixture was cooled to room temperature and poured into 600 mL of ethanol. The precipitate was filtered, washed with water, dried in vacuo, and reprecipitated using a THF–methanol system. Small amounts of THF-insoluble product were removed by a micropore filter (pore size: 0.5 μm). Drying in vacuo for 8 h gave 520 mg of pale yellow polymer 1 (4% yield). This polymerization procedure was also used with different solvents.

The resulting polymer was soluble in THF, DMF, and even in *m*-bis(trifluoromethyl)benzene. A thin film of polymer 1 was more water repellent than thin films of ordinary organopolysilanes. The refractive index of this polymer film was $n^{20}{}_D = 1.545$.

Characterization. Elemental analyses for C and H were carried out using a Heraeus CHN-rapid automatic elemental analysis instrument. A Hitachi 3500 double-beam spectrophotometer was used to record UV absorption spectra, and the IR spectrum was accumulated on a Perkin-Elmer FT-IR spectrophotometer. The distribution of molecular weights was evaluated by gel permeation chromatography (GPC) using a Tosoh HLC837 automatic analyzer (column, TSK gel GMH6 + TSK gel

G4000H8; calibration, polystyrene standard; eluant, THF; wavelength of UV detector, 254 nm). NMR spectra for ^{1}H, ^{13}C, ^{19}F, and ^{29}Si were obtained with a Varian Gemini 200 or Unity 400 FT-NMR spectrometer at room temperature (^{1}H, 200.06 MHz; ^{13}C, 50.29 MHz; ^{19}F, 376.29 MHz; ^{29}Si, 79.46 MHz). $(CH_3)_4Si$ was used as an internal standard for ^{1}H, ^{13}C, and ^{29}Si NMR spectra, and $CFCl_3$ was used for ^{19}F NMR spectra. The thermochromic behavior of a solid film of polymer 1 spin-coated on a quartz plate was measured in a cryostat (10^{-5} Torr) using a Hitachi U-3200 spectrophotometer. Thermal gravimetric (TG) analysis was performed using a Shimadzu TGA-50, and differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC7. The glass transition temperature was evaluated by determining the temperature at which the DSC base line began to shift when the polymer was heated (40 °C/min) from −190 to +150 °C. Refractive index was measured by an Abbe refractometer (Atago NAR-1T, Japan).

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References and Notes

(1) (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) Fujino, M.; Matsumoto, N.; Ban, H.; Sukegawa, K. *J. Polym. Sci., Polym. Lett.* **1988**, *26*, 109.

(2) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352.

(3) (a) Fujino, M. *Chem. Phys. Lett.* **1987**, *136*, 451. (b) Kepler, R. G.; Zeigler, J. M.; Harrar, L. A.; Kurtz, S. R. *Phys. Rev. B* **1987**, *35*, 2818. (c) Abkowitz, M.; Knier, F. E.; Yuh, H.-J.; Weagley, R. J.; Stolka, M. *Solid State Commun.* **1987**, *62*, 547.

(4) Yang, L.; Wang, Q. Z.; Ho, P. P.; Dorsinville, R.; Alfano, R. R. *Appl. Phys. Lett.* **1988**, *53*, 1245.

(5) (a) Kagawa, T.; Fujino, M.; Takeda, K.; Matsumoto, N. *Solid State Commun.* **1986**, *57*, 635. (b) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601.

(6) (a) Kawai, H. *Jpn. J. Appl. Phys.* **1969**, *8*, 975. (b) Furukawa, T.; Date, M.; Fukada, E. *J. Appl. Phys.* **1980**, *51*, 1135. (c) Kakuchi, M.; Sugawara, S.; Murase, K.; Matsuyama, K. *J. Electroanal. Soc.* **1977**, *124*, 1648.

(7) Trujillo, R. E. *J. Organomet. Chem.* **1980**, *198*, C27.

(8) Fujino, M.; Hisaki, T.; Fujiki, M.; Matsumoto, N. International Symposium on Organosilicon Chemistry Directed Towards Material Science, Sendai, Japan, 1990, Abstract P213.

(9) Fujino, M., unpublished results. For instance, the yield of methylphenylpolysilane (MPhPSi) increased monotonically as the reaction temperature increased. Polymerization at the refluxing temperature in octane (bp 126 °C) yielded 11% MPhPSi; in dodecane (bp 215 °C), it yielded 50% MPhPSi.

(10) Fujino, M., unpublished results. For example, the yield of dihexylpolysilane was increased from 0.05% to 11% by 30 min polymerization using 7:3 toluene/diglyme instead of only toluene. A 34% yield for 5 h of polymerization is also reported in ref 11.

(11) Rabolt, J. R.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611.

(12) Fujino, M.; Isaka, H. *J. Chem. Soc., Chem. Commun.* **1989**, 466.

(13) This unknown polymer did not have the UV absorption maximum around 300 nm that would have indicated a long linear catenation of Si–Si bonding. Polymerization conditions were as follows: temperature, 155–162 °C; solvent, 100 mL of *n*-decane; time, 5 h; (3,3,3-trifluoropropyl)methyldichlorosilane (0.0948 mol) and 18-crown-6 (0.009 48 mol). The yield of the unknown polymer was 0.6%, and its molecular weight was 35 000 ($M_w/M_n = 2.0$).

(14) Found: C, 34.06%; H, 5.17%. Calcd for $(C_4H_7SiF_3)_n$: C, 34.27%; H, 5.03%.

(15) Characteristic absorption bands are as follows: ν_{C-H}, 2956, 2908; ν_{Si-H}, 2060–2180; $\nu_{CH=CF_2}$, 1856; δ_{C-H}, 1440; δ_{Si-Me}, 1264; $\delta_{Si-CH_2CH_2CF_3}$, 1206, 1128, 1066, 1026, 894.

(16) For example, $\delta(^{19}F) = 61.68$ ppm for CF_3CH_3, 68.94 ppm for $CF_3CH_2CH_3$, and 65.68 ppm for $CF_3(CH_2)_4CF_3$ were reported in ref 17.

(17) Elleman, D. D.; Brown, L. C.; Williams, D. J. *J. Mol. Spectrosc.* **1961**, *7*, 307, 322.

(18) The ^{29}Si NMR chemical shifts of dichlorosilanes are as follows: $CF_3CH_2CH_2(CH_3)SiCl_2$, −63.327 ppm; $CH_3CH_2CH_2(CH_3)SiCl_2$, −64.685 ppm.

(19) The ^{29}Si NMR chemical shift of MPrPSi was −32.56 ppm, and the peak showed fine structure. The fine structure coincides with those reported in ref 20.

(20) Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2309.

(21) ^{1}H and ^{13}C NMR chemical shifts of $CF_3CH_2CH_2(CH_3)SiCl_2$ in $CDCl_3$ were as follows: $\delta(^{1}H) = 0.814$ ppm ($SiCH_3$), 1.330 ppm ($SiCH_2$), and 2.252 ppm (CH_2CF_3); $\delta(^{13}C) = 4.824$ ppm ($SiCH_3$), 14.035 ppm ($SiCH_2$), 27.867 ppm (q, CH_2CF_3, $J_{C2-F} = 31.130$ Hz), and 127.156 ppm (q, CF_3, $J_{C3-F} = 275.841$ Hz).

(22) (a) Takeda, K.; Teramae, H.; Matsumoto, N. *J. Am. Chem. Soc.* **1986**, *108*, 8186. (b) Takeda, K.; Fujino, M.; Seki, K.; Inokuchi, H. *Phys. Rev. B* **1987**, *36*, 8129.

(23) (a) Mintmire, J. W. *Phys. Rev. B* **1989**, *39*, 13350. (b) Teramae, H.; Takeda, K. *J. Am. Chem. Soc.* **1989**, *111*, 1281.

(24) Natta, G. *Macromol. Chem.* **1960**, *35*, 94.

(25) This cyclic compound was identified from its mass spectrum. The low molecular weight compounds, including this cyclic compound, separated into a liquid layer below the mother liquor when the reaction mixture was cooled to room temperature.