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## **SYNTHESIS OF $\alpha,\omega$ -BIFUNCTIONAL FLUORINE-CONTAINING POLYSILOXANES BY HYDROSILATION REACTION**

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### **ABSTRACT**

$\alpha,\omega$ -Bis(trifluoroacetamide)-terminated polysiloxanes containing Si—H bonds were prepared by cationic equilibration reaction of the cyclic tetramers, octamethylcyclotetrasiloxane and 1,3,5,7-tetramethylcyclotetrasiloxane, and bis(3-aminopropyl)tetramethyldisiloxane, catalyzed by trifluoroacetic acid. The pendant Si—H silane bonds were then added quantitatively to 3,3,4,4,5,5,5-heptafluoro-1-pentene by using chloroplatinic acid catalysis. The end groups of these fluorine-containing polysiloxanes were then hydrolyzed to unprotected primary amino groups. Carboxyl- or hydroxyl-terminated polysiloxanes were also prepared by similar methods. Fluorine-containing siloxane-urea segmented copolymers were synthesized by using  $\alpha,\omega$ -diamino-terminated polysiloxanes.



introduce fluorine into siloxane segments since surface properties or water or oxygen permeabilities can be improved. By using these fluorine-containing polysiloxanes, siloxane-urea segmented copolymers were easily prepared by solution polymerization, and the results are described in this paper.

## EXPERIMENTAL

### Materials

Octamethylcyclotetrasiloxane (**1**) and 1,3,5,7-tetramethylcyclotetrasiloxane (**2**) were products of Petrarch Systems Inc. Bis(3-aminopropyl)tetramethyldisiloxane (**3**), bis(3-carboxypropyl)tetramethyldisiloxane (Silar Laboratories Inc.), and 3,3,4,4,5,5,5-heptafluoro-1-pentene (PCR Research Chemicals Inc.) were also commercially available. 4,4'-Dicyclohexylmethane diisocyanate (H-MDI) was kindly supplied by Miles Chemical Co. Solvents such as tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were distilled under argon atmosphere prior to use.

### Preparation of Polysiloxanes with Si—H Bonds

As a typical example, an  $\alpha,\omega$ -bis(trifluoroacetamide)-terminated polysiloxane with Si—H bonds (**4**) was prepared as follows. The acid-catalyzed equilibration reaction of **1** and the second silane containing monomer (**2**) was carried out in the presence of bis(3-aminopropyl)-tetramethyldisiloxane (**3**) by using trifluoroacetic acid as a catalyst. Sufficient catalyst was employed in concentrations adequate to first cap the amine terminals (equimolar to amino groups) and to subsequently open the rings (5 mol% of Si—O bonds). The reaction mixture was stirred under argon atmosphere at 80°C for 30 hours. The resulting viscous liquid was washed with distilled water repeatedly to remove the excess acid catalyst. Volatile cyclic siloxane oligomers were stripped by distillation under reduced pressure to produce a viscous colorless liquid having structure **4**. Polysiloxanes with carboxyl- (**7**) or trifluoroacetoxy- (**9**) end groups were also prepared by methods similar to those described above.

### Hydrosilation and Hydrolysis Reactions

These reactions were conducted as follows. Under an argon atmosphere, 3,3,4,4,5,5,5-heptafluoro-1-pentene and chloroplatinic acid catalyst in THF were stirred at 7°C for 30 minutes in a closed system. Next, a THF solution of polysiloxane (**4**) was added slowly from a dropping funnel at room temperature (23°C) over a period of 2 hours. When half of the calculated amount of **4** was added, further fluoroolefin and Pt catalyst were added. After complete addition, the reaction mixture was stirred for 2 hours at room temperature and then for an additional 4 hours at 35°C. The insoluble fraction was filtrated, and a brown viscous liquid was obtained after evaporation of THF. After treatment with activated carbon three times, a light yellow liquid of  $\alpha,\omega$ -bis(trifluoroacetamide)-terminated fluorine-containing polysiloxane (**5**) was obtained.

The end groups of the oligomer **5** were hydrolyzed by  $\text{Na}_2\text{CO}_3$  in the THF-water system at  $70^\circ\text{C}$  for 48 hours to produce  $\alpha,\omega$ -diamino-terminated fluorine-containing polysiloxane copolymer (**6**).

Hydrosilation reactions of **7** and **9** with heptafluoropentene and hydrolysis of end trifluoroacetoxy group in **10** were successfully conducted under similar conditions.

### Segmented Copolymerization

H-MDI was stirred in dry DMF at room temperature under an argon atmosphere. Aminopropyl-terminated polysiloxane (**6**) in DMF was added from a dropping funnel. After complete addition, the mixture was stirred at  $50^\circ\text{C}$  for 4 hours. The resulting copolymer was isolated by coagulation into a mixture of methanol and water (80:20, v/v) and washing with methanol several times and then drying in vacuo at  $60^\circ\text{C}$  overnight.

### Characterization

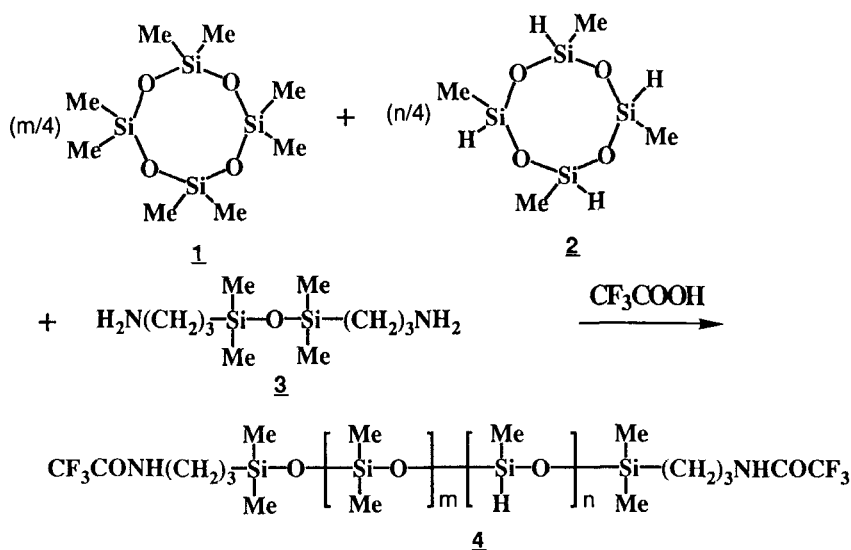
All polymers obtained here were characterized by FT-IR and  $^1\text{H-NMR}$  spectra. FT-IR spectra were obtained with a Nicolet MX-1. The  $^1\text{H-NMR}$  spectra were obtained using a Varian EM-390 (90 MHz) with an approximately 10% solution of the polysiloxanes in chloroform-*d*. Dichloromethane was an internal reference. Thermal characterizations were performed on a Perkin Elmer System 2. DSC scans were recorded under helium atmosphere with a heating rate of  $10^\circ\text{C}/\text{min}$ . Potentiometric titration of **6** was carried out in isopropanol by using HCl as titrant and bromophenol blue as an indicator.

## RESULTS AND DISCUSSION

An  $\alpha,\omega$ -bis(trifluoroacetamide)-terminated polysiloxane oligomer (**4**) was prepared according to Scheme 2. The results of the preparation of **4** are summarized in Table 1. Oligomer **4** is a colorless viscous liquid which is soluble in common organic solvents such as THF, dichloromethane, and chloroform.

As a typical example, Fig. 1 shows the  $^1\text{H-NMR}$  spectrum of **4** in the case of Run 4 in Table 1. The number-average molecular weight was estimated from this spectrum. That is, by determining the integral ratio of the methylene terminal group (**a** in Fig. 1) to the silicon methyl (**b**) in-chain groups, the molecular weight of **4** was calculated as 480. This value was close to that target molecular weight (500), which was calculated from the molar feed ratio. This result shows that the molecular weight can be easily controlled by changing the ratio of **1** and **2** to the bis(3-aminopropyl)tetramethyldisiloxane (**3**).

Hydrosilation reactions of **4** were conducted in THF with 3,3,4,4,5,5,5-heptafluoro-1-pentene as shown in Scheme 3. Although a small fraction of gel was formed, a soluble viscous liquid of **5** was produced effectively. The reaction was monitored by FT-IR spectra, which are illustrated in Fig. 2. The top spectrum in Fig. 2 shows the starting polysiloxane (**4**), which contains Si-H absorption at 2160



SCHEME 2.

$\text{cm}^{-1}$ . This band disappeared after the reaction, and several new bands near 1200–1400  $\text{cm}^{-1}$  due to the  $\text{C}_3\text{F}_7$  group appeared in **5**.

Hydrolysis of the trifluoroacetamide end group of **5** was achieved via reaction with aqueous  $\text{Na}_2\text{CO}_3$  in THF at room temperature. As shown in Fig. 2, the  $\text{C}=\text{O}$  absorption of the amide group at 1678  $\text{cm}^{-1}$  also decreased and the  $\text{N}-\text{H}$  stretching band for the primary amine appeared around 3300  $\text{cm}^{-1}$ .

The structure of **6** was supported not only by FT-IR but also by the  $^1\text{H-NMR}$  spectrum. As a typical sample, the  $^1\text{H-NMR}$  spectrum of **6**, which was prepared

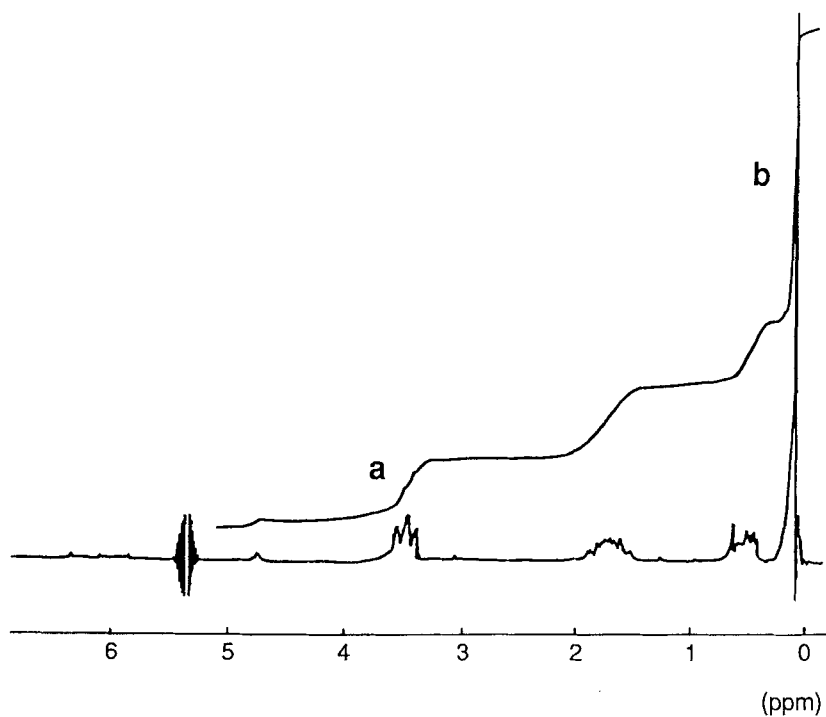
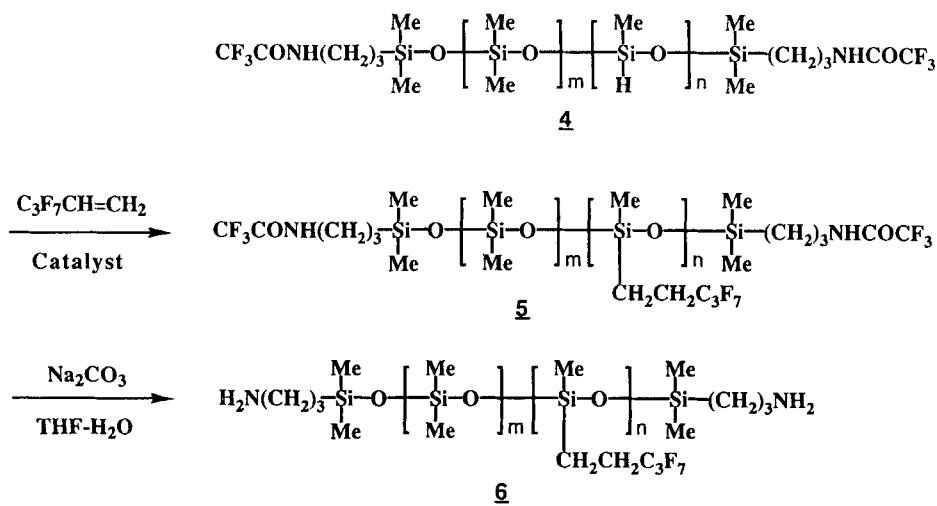
TABLE 1. Preparation of  $\alpha,\omega$ -Bis(trifluoroacetamide) Siloxane Copolymers

Run	[1]/[2] <sup>a</sup>	[1 + 2]/[3] <sup>a</sup>	Target <sup>b</sup> molecular weight	Yield, <sup>c</sup> %
1	3	9.77	3000	47
2	3	6.18	2000	34
3	3	2.03	1000	30
4	3	0.25	500	26
5	5	8.98	3000	58
6	5	6.08	2000	62
7	0.33	10.12	3000	69

<sup>a</sup>Molar ratio.

<sup>b</sup>Calculated from the feed ratio.

<sup>c</sup>Isolated yield.

FIG. 1.  $^1\text{H}$ -NMR spectrum of 4.

SCHEME 3.

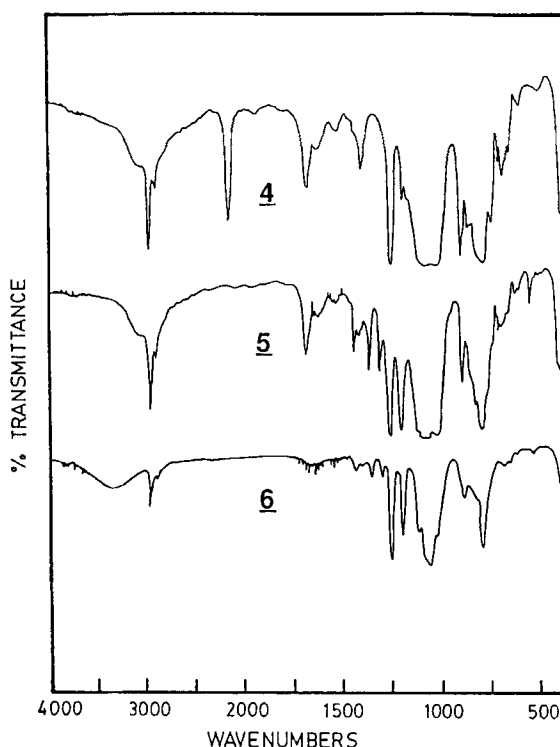


FIG. 2. FT-IR spectra of **4**, **5**, and **6**.

from **4** (Run 7 in Table 1), is shown in Fig. 3. The methylene peaks from the groups adjacent to  $C_3F_7$  group are shown at  $\delta$  3.5 and 1.7. From the integral ratio of these methylene groups (for example, **a** in Fig. 3) to the methyl protons (**b**), the ratio of dimethylsilyl to monomethylsilyl groups in **6** can be calculated. This value (0.355) is very close to that (0.333) calculated from the feed ratio of **1** and **2**. This result suggests that the introduction of the perfluoroalkyl group to polysiloxane by hydrosilation reaction succeeded almost quantitatively.

The results of preparation of **6** are summarized in Table 2. For example, the titration of the amino end group of **6** (Run 3 in Table 2) by alcoholic HCl showed its molecular weight was 2750. This sample was prepared starting from **4** (Run 6 in Table 1) and its calculated molecular weight by using target molecular weight (2000) of **4** was 2520. The proximity of these two values supports the view that the hydrolysis of **5** to **6** proceeded effectively.

Similarly to **4**, carboxyl (**7**) or trifluoroacetoxy-terminated polysiloxanes (**9**) with Si—H bonds were easily prepared by using bis(3-carboxypropyl)tetramethyldisiloxane or bis(4-hydroxybutyl)tetramethyldisiloxane, respectively. These polysiloxanes were also hydrosilated with heptafluoropentene to produce end-reactive fluorine-containing polysiloxanes (**8** and **10**). The end trifluoroacetoxy groups were hydrolyzed to unprotected hydroxy groups (**11**). These reactions are summarized in Schemes 4 and 5. As shown in Fig. 4, FT-IR spectra support the structures of **8**



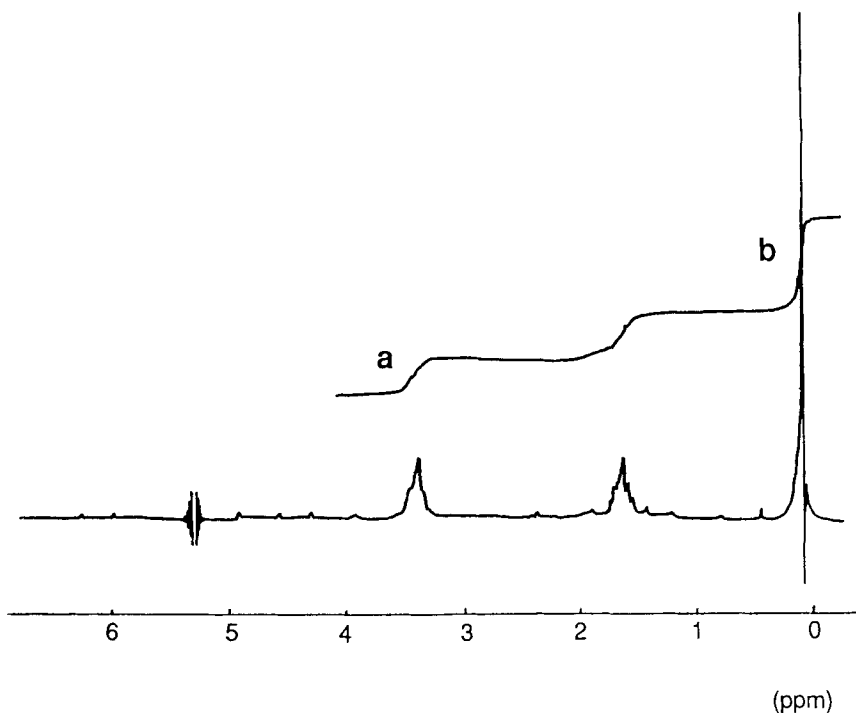


FIG. 3.  $^1\text{H-NMR}$  spectrum of **6**.

and **11**. Thus, various end-reactive fluorine-containing polysiloxanes were easily prepared by this method.

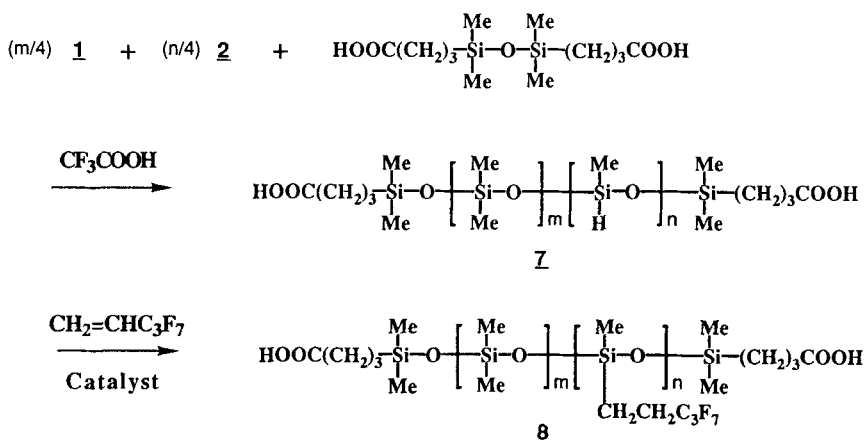
Glass transition temperature values ( $T_g$ ) of fluorine-containing polysiloxanes (**5**, **6**, **8**, and **11**) are given in Table 3. Compared with the  $T_g$  of  $-123^\circ\text{C}$  for the poly(dimethylsiloxane) homopolymer,  $T_g$  of these polysiloxane copolymers is increased by the incorporation of the perfluoroalkyl group into polysiloxanes. How-

TABLE 2. Preparation of **5** and **6**

Run	<b>4</b>		<b>5</b>		<b>6</b>		
	Target molecular weight	$m:n$	Yield, <sup>a</sup> %	Calculated <sup>b</sup> molecular weight	Yield, <sup>a</sup> %	Calculated <sup>b</sup> molecular weight	Titrated molecular weight
1	3000	1:3	18	8930	15	8740	9210
2	3000	3:1	40	4780	32	4590	5160
3	2000	5:1	26	2710	28	2520	2750
4	3000	5:1	31	4170	28	3980	4100

<sup>a</sup>Based on **4**.

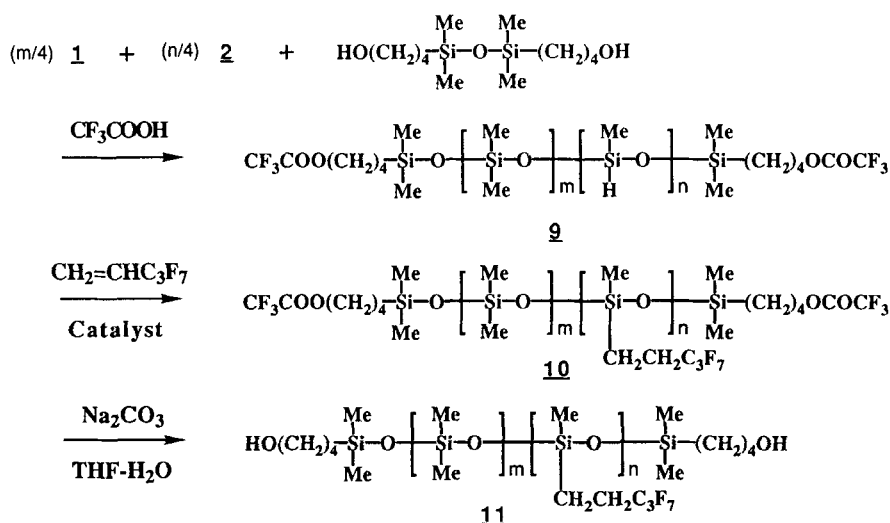
<sup>b</sup>Calculated from the target molecular weight of **4**.



SCHEME 4.

ever, as can be seen in Table 3, the glass transition temperatures of all these polysiloxanes are still very low.

$\alpha,\omega$ -Diamino-terminated fluorine-containing polysiloxanes (**6**) can be used for the preparation of segmented copolymers. For example, **6** ( $M_n = 2750$ ) was reacted with an equimolar H-MDI to produce a siloxane-urea copolymer (**12**) as shown in Scheme 6. During the reaction, the solutions appeared to be homogeneous and **12** was isolated as a white solid. Yield of **12** was 82%. The intrinsic viscosity of **12** in DMF at 25°C was 0.24 (dL/g). The FT-IR spectrum of **12** is shown in Fig. 5. The strong absorptions at 3350  $\text{cm}^{-1}$  ( $\nu\text{N-H}$ ) and 1633  $\text{cm}^{-1}$  ( $\nu\text{C=O}$ ) confirm the formation of urea linkages. The disappearance of the peak at 2273  $\text{cm}^{-1}$  ( $\nu\text{NCO}$ )



SCHEME 5.

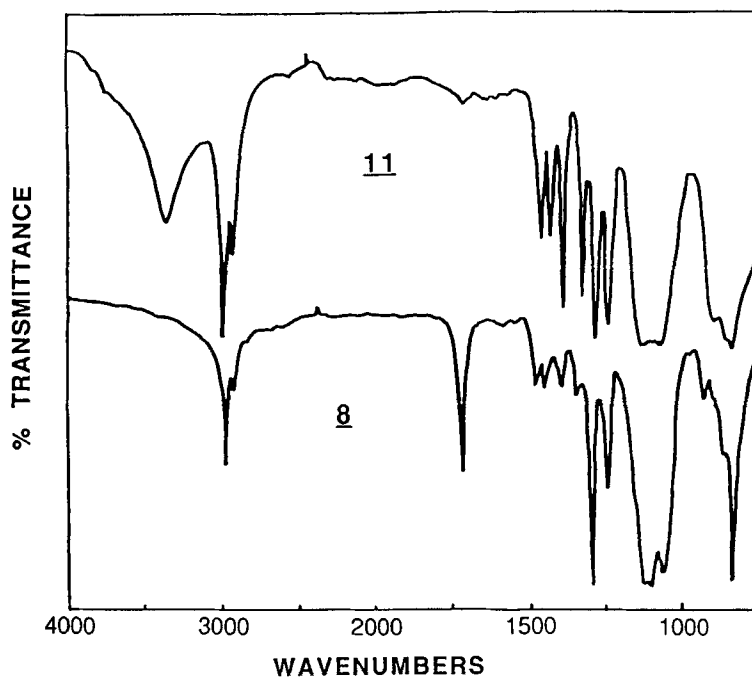
FIG. 4. FT-IR spectra of **8** and **11**.

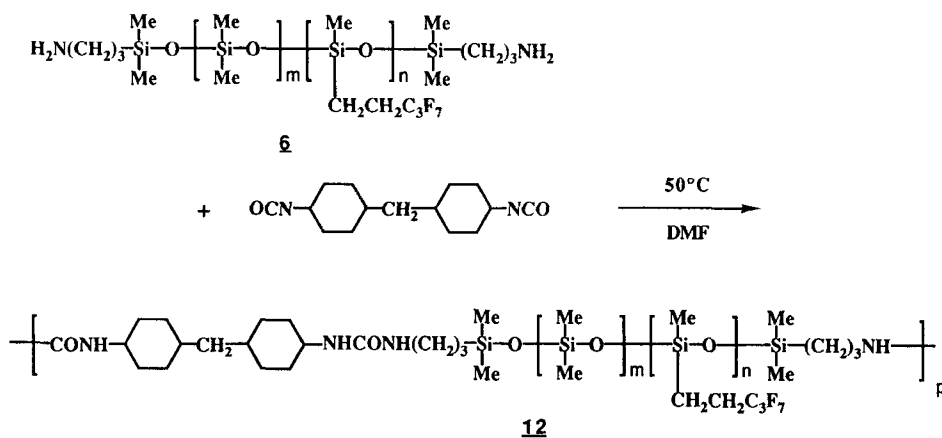
TABLE 3. Glass Transition Temperatures of Fluorine-Containing Polysiloxanes

$$\text{X(CH}_2\text{)}_3\text{—Si} \begin{array}{c} \text{Me} \\ | \\ \text{—O—} \\ | \\ \text{Me} \end{array} \text{—} \left[ \begin{array}{c} \text{Me} \\ | \\ \text{—Si—O—} \\ | \\ \text{Me} \end{array} \right]_m \text{—} \left[ \begin{array}{c} \text{Me} \\ | \\ \text{—Si—O—} \\ | \\ \text{CH}_2\text{CH}_2\text{C}_3\text{F}_7 \end{array} \right]_n \text{—} \begin{array}{c} \text{Me} \\ | \\ \text{—Si—} \\ | \\ \text{Me} \end{array} \text{—(CH}_2\text{)}_3\text{X}$$

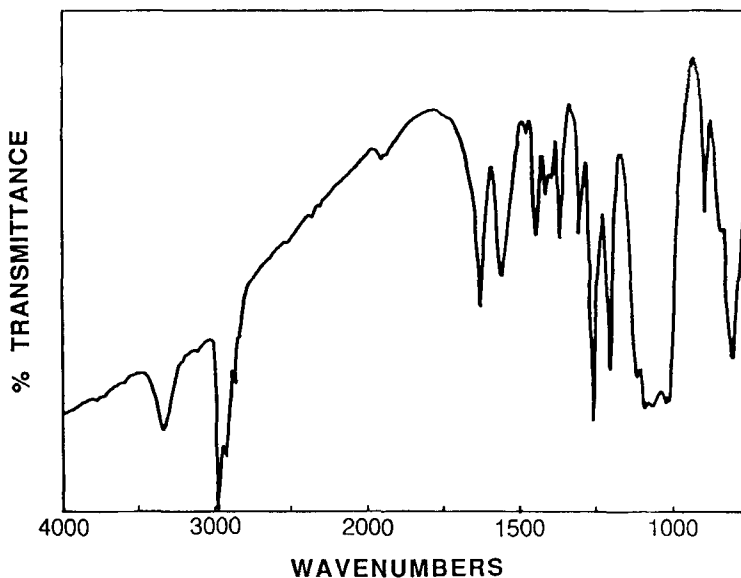

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Run	End-group X	Molecular weight		<i>m</i> : <i>n</i>	$\begin{array}{c} \text{Me} \\   \\ \text{—Si—O—} \\   \\ \text{CH}_2\text{CH}_2\text{C}_3\text{F}_7 \\ \text{wt}\% \text{ }^a \end{array}$	<i>T<sub>g</sub></i> , <sup>b</sup> °C
		Calculated	Titred			
1	CF <sub>3</sub> CONH—	4780		3:1	54	−84
2	H <sub>2</sub> N—	8740	9210	1:3	91	−65
3	H <sub>2</sub> N—	4590	5160	3:1	54	−79
4	HOCH <sub>2</sub> —	4570		3:1	54	−84
5	HOOC—	4870		3:1	54	−88

<sup>a</sup>Without end groups.<sup>b</sup>By DSC, 10°C/min.



SCHEME 6.


 FIG. 5. FT-IR spectrum of **12**.

supports the complete reaction of isocyanate group. Also, the peaks around  $1000\text{--}1400\text{ cm}^{-1}$  demonstrate the incorporation of the siloxane and fluoroalkyl groups into the copolymer.

In conclusion,  $\alpha,\omega$ -bifunctional fluorine-containing polysiloxanes were easily prepared and used for the segmented copolymerization. Studies of the physical properties of these fluorine-containing polysiloxanes and their copolymers are now under investigation.

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