Reactivity of Cyclosiloxane with 3,3,4,4,5,5,6,6,6-Nonafluorohexyl Group and Its Application to Fluorosilicone Synthesis

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ABSTRACT: The reactivity of cyclosiloxane with 3,3,4,4,5,5,6,6,6-nonafluorohexyl group and its application to fluorosilicone synthesis were studied. In contrast to the polymerization of the commercially available 1,3,5-tris(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane (CF_3–D3), the polymerization of 1,3,5-tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,3,5-trimethylcyclotrisiloxane (C_4F_9–D3) with sodium hydroxide yielded 1,3,5,7-tetrakis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane {$[C_4F_9CH_2CH_2(CH_3)SiO]_4$ (C_4F_9–D4)} as the major product, which was the result of the depolymerization by a backbiting mechanism. On the other hand, the polymerization of C_4F_9–D3 with trifluoromethanesulfonic acid yielded a polymer with good reproducibility, although the distribution of molecular weight tended to be bimodal. C_4F_9–D3 was also successfully copolymerized with octamethylcyclotetrasiloxane (D4). The properties of the obtained copolymers changed almost linearly with the amount of $[C_4F_9C_2H_4(CH_3)SiO]$ units, except for the surface tension. The surface tension of the copolymer containing more than 50% $[C_4F_9C_2H_4(CH_3)SiO]$ units by weight was almost as low as that of the homopolymer. When the copolymer containing 50% $[C_4F_9C_2H_4(CH_3)SiO]$ units by weight was examined for an antifoaming agent, it worked as effectively as the homopolymer in the toluene foaming system. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3333–3340, 2001

Key words: fluorosilicone; 3,3,4,4,5,5,6,6,6-nonafluorohexyl group; reactivity of fluorinated cyclosiloxane; copolymerization of fluorinated cyclosiloxane

INTRODUCTION

Poly(3,3,3-trifluoropropylmethylsiloxane) (PTFPMS) is widely used as the principal constituent of various kinds of silicone products by virtue of its unique properties not obtained in poly(dimethylsiloxane) (PDMS).[1] However, PTFPMS has been shown to be insufficient to take advantage of the features of fluoropolymers, which include the low surface tension property and the fuel- and oil-resistant nature.[2] These properties may be improved by introducing a longer perfluoroalkyl side chain to a siloxane backbone.[3]

Although some synthetic methods are possible as a means for obtaining fluorosilicone, the ring opening polymerization of a cyclosiloxane is the most important method as it is for organopolysiloxanes, which have only unsubstituted hydrocarbon groups, particularly when a fluo-
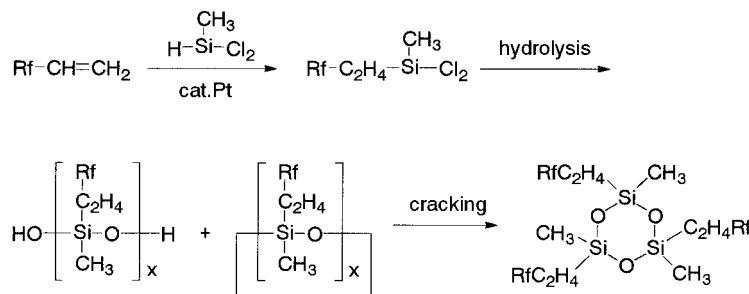
Scheme 1 Synthesis of fluorine-containing cyclotrisiloxane.

rosilicone rubber gum with high molecular weight or a fluorosilicone polymer with controlled molecular weight is required. This method involves hydrosilylation between a perfluoroalkyl ethylene and a methyl dichlorosilane to yield a 2-perfluoroalkylethyl methyl dichlorosilane, which is hydrolyzed to give either a linear or a cyclo oligomer. These oligomers are then transformed into a cyclotrisiloxane by the method referred to as "cracking." In this reaction either a linear or a cyclo oligomer is heated in the presence of the alkaline catalyst and transformed into a cyclotrisiloxane by distilling a cyclotrisiloxane generated in a reactor. Thus, a cyclotrisiloxane with a long fluoroalkyl side chain is difficult to obtain because its boiling point is too high (Scheme 1). Actually, our experiments suggested that the 3,3,4,4,5,5,6,6,6-nonafluorohexyl group ($C_4F_9C_2H_4-$) was the longest fluoroalkyl group employed in this method. Poly(3,3,4,4,5,5,6,6,6-nonafluorohexylmethylsiloxane) (PNFHMS) was synthesized by the ring opening polymerization of 1,3,5-tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,3,5-trimethylcyclotrisiloxane (C_4F_9–D3) and studied from the viewpoint of its surface tension.[4]

However, the reactivity of C_4F_9–D3 remained unknown and the copolymerization between C_4F_9–D3 and cyclodimethylsiloxane was not investigated. The copolymer can be expected to provide a flexible property–cost balance, combining the features of fluoropolymers with the economics of PDMS.

In this context, we studied the reactivity of C_4F_9–D3 toward a base or acid catalyst. In addition, the copolymerization of C_4F_9–D3 and D3 or D4 was studied. The properties of the synthesized oils and their application to an antifoaming agent are also reported.

EXPERIMENTAL

Materials

3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexene ($C_4F_9CH=CH_2$) was used as obtained from Asahi Glass Co. (Kanagawa, Japan). Hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), hexamethyldisiloxane (MM), methyldichlorosilane, trimethylchlorosilane, and 1,3,5-tris(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane (CF_3–D3) were purchased from Shin-Etsu Chemical Co. (Japan) and used as delivered. C_4F_9–D3 was synthesized as previously reported,[5] except that cesium hydroxide was used instead of potassium hydroxide for the alkaline catalyst of the cracking process. In our experiment, the use of cesium hydroxide gave C_4F_9–D3 in a better yield (90.7%) than that of potassium hydroxide (70.2%). Trifluoromethanesulfonic acid was purchased from Kanto Chemical Co. (Japan), and used as delivered. Surflon S-382 (the surface-active agent containing a fluorinated acrylate polymer) and 1,3-bis(trifluoromethyl)benzene were obtained from Seimi Chemical Co. (Japan) and used as delivered. The other chemicals and solvents were purchased as reagent-grade materials.

Characterizations

^{1}H NMR spectra were recorded at 300 MHz on a JEOL JNM-AL300 spectrometer (JEOL Ltd., Japan) using $CDCl_3$ or mixtures of $CDCl_3$ and trichlorotrifluoroethane (F113) as a solvent. ^{19}F NMR spectra were also recorded at 300 MHz on a JEOL JNM-AL300 spectrometer with $CDCl_3$ or mixtures of $CDCl_3$ and F113 as a solvent and $CFCl_3$ as an internal reference. IR spectra were obtained on a Jasco IR-810 spectrometer (Jasco Corp., Japan). Gas chromatographic analyses were performed on a Shimadzu GC-15A (Shi-

madzu, Japan) equipped with a TCD detector. Gel permeation chromatography (GPC) was carried out in 1,3-dichloro-1,1,2,2,3-pentafluoropropane containing hexafluoroisopropanol (1 vol %) on a Tosoh HLC-8020 chromatograph equipped with two polystyrene gel columns (PLgel Mixed-C column) and a refractive index detector (Tosoho Corp., Japan). Molecular weights of the polymers were calibrated with perfluoropolyether standards.

Measurements

The equilibrium liquid surface tension was measured with a Kyowa Interface Science Company (Japan) ESB-V surface tensiometer at 25°C, using a Wilhelmy platinum plate. The refractive index was obtained with an Atago model 2T refractometer (Japan) and the density with a small pycnometer. The viscosity was measured with an Ubbelohde viscometer or a rotary viscometer (Tokyo Keiki Co., Japan) at 25°C. The dielectric constant was measured with an ADP-203 model (Ando Electric Co., Japan). The melting point was determined on a Buchi-530 model (Buchi Laboratoriums, Technik AG, Germany).

Polymerization of C$_4$F$_9$–D3 with Sodium Hydroxide (Typical Procedure)

A 200-mL three-necked flask equipped with a stirrer and a thermometer was sufficiently replaced by nitrogen and was charged with C$_4$F$_9$–D3 (100 g). After raising the temperature to 150°C, sodium hydroxide (3 mg) was added. The progress of the polymerization was monitored with a torque meter. After 4 h, the GC analysis of the reaction mixture revealed the disappearance of C$_4$F$_9$–D3. The product was distilled to yield 74.3 g (74.3%) of C$_4$F$_9$–D4 as the mixtures of stereoisomers: bp 168–172°C (3 mmHg); mp 33.2–34.8°C; IR 2966, 2914, 1268, 1218, 1133, 1082, 879, 843 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.16–0.27 (3H), 0.76–0.90 (2H), 1.96–2.19 (2H); ^{19}F NMR (CDCl$_3$) δ: −81.1 to −81.5 (3F), −116.0 to −116.7 (2F), −124.2 to −124.7 (2F), −125.8 to −126.3 (2F).

Polymerization of C$_4$F$_9$–D3 with Potassium Hydroxide in the Presence of the Phase-Transfer Catalyst

A 500-mL three-necked flask equipped with a stirrer and a thermometer was sufficiently replaced by nitrogen and was charged with C$_4$F$_9$–D3 (100 g). At the temperature of 20°C, potassium hydroxide (4.2 mg) and 18-*crown*-6 (19.8 mg) was added. The progress of the polymerization was monitored with a torque meter. When the torque reached the maximum value, trimethylchlorosilane (16.3 mg) was introduced to terminate the reaction. The quenched reaction mixture was diluted with 1,3-dichloro-1,1,2,2,3-pentafluoropropane (∼ 200 mL) and filtrated to remove the metal-containing residues. The filtrate was evaporated. Stripping of the volatile siloxanes was done at 180°C under reduced pressure at 3 mmHg for 2 h to give the product. The viscosity of the product was 10,000,000 cps: ^{1}H NMR (CDCl$_3$) δ: 0.16–0.27 (3H), 0.76–0.90 (2H), 1.96–2.19 (2H); ^{19}F NMR (CDCl$_3$) δ: −81.1 to −81.5 (3F), −116.0 to −116.7 (2F), −124.2 to −124.7 (2F), −125.8 to −126.3 (2F).

Copolymerization of Cyclotrisiloxanes with Trifluoromethanesulfonic Acid (Triflic Acid) (Typical Procedure)

A 500-mL three-necked flask equipped with a stirrer and a thermometer was sufficiently replaced by nitrogen and was charged with C$_4$F$_9$–D3 (100 g), D4 (100 g), and MM (3.6 g). After raising the temperature to 50°C, trifluoromethanesulfonic acid (0.1 g) was added. Five hours later, extinction of C$_4$F$_9$–D3 was confirmed by gas chromatography, and sodium bicarbonate (1.1 g) was introduced to terminate the reaction. After stirring for 1 h, filtration was carried out at a pressure of 1 kgf/cm^2 to obtain a transparent oil. Stripping of the volatile siloxanes was done at 180°C under reduced pressure at 3 mmHg for 2 h.

Kinetics

A 100-mL three-necked flask equipped with a stirrer and a thermometer was sufficiently replaced by nitrogen and was charged with a cyclosiloxane (10–50 g). When the temperature of the flask was adjusted to 75°C, trifluoromethanesulfonic acid (0.03 mol %) was added. Samples (0.1 g) were withdrawn from time to time and 1,3-bis(trifluoromethyl)benzene (0.5 g) was added. The solutions were analyzed for the amount of the unchanged cyclosiloxane by gas chromatography with 1,3-bis(trifluoromethyl)benzene as an internal reference. The reactivity of each cyclosiloxane toward trifluoromethanesulfonic acid was evaluated by the rate of 10% conversion of each cyclosiloxane.

Antifoam Tests

Organic foaming surfactant solutions were prepared by adding the surfactant (Surflon S-382) to toluene or tetrachloroethylene at the concentration of 0.5 wt %. Antifoaming compound (10 g) was mixed with 1,3-bis(trifluoromethyl)benzene (100 g). This solution (0.1 g) was added to the organic foaming surfactant solution (100 g) in a 200-mL sample tube. The tube was shaken for 1 min. The antifoaming efficiency was determined by observing the collapse of the foam.

RESULTS AND DISCUSSION

Reactivity of C_4F_9–D3

Poly(dimethylsiloxane) (PDMS) is obtained by the ring opening polymerization of $[(CH_3)_2SiO]_x$ (where x is 3–5), or the condensation polymerization of the hydrolysis products of dimethyldichlorosilane. A base or an acid catalyzes both. The yield of the polymer is generally high because its equilibrium favors polymer formation.

On the other hand, it is possible to obtain the appreciable yield of PTFPMS only by the ring opening polymerization of CF_3–D3 in the presence of either a base or an acid as a catalyst. When PTFPMS with high molecular weight is required, a base catalyst is selected. The polymerization must be terminated before the equilibrium is reached, because its equilibrium disfavors the formation of polymer.

Polymerization of C_4F_9–D3 with Sodium Hydroxide

The ring opening polymerization of CF_3–D3 is usually carried out in the range from 150 to 200°C
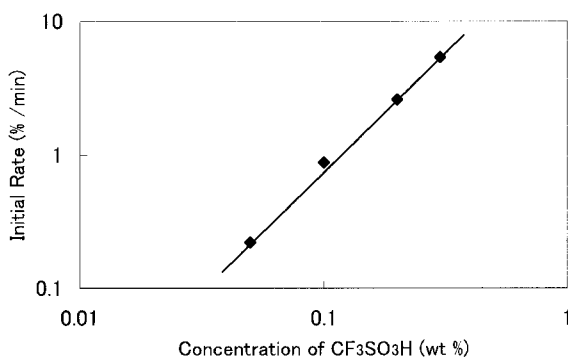
Figure 1 Dependence of the initial rate of the polymerization of C_4F_9–D3
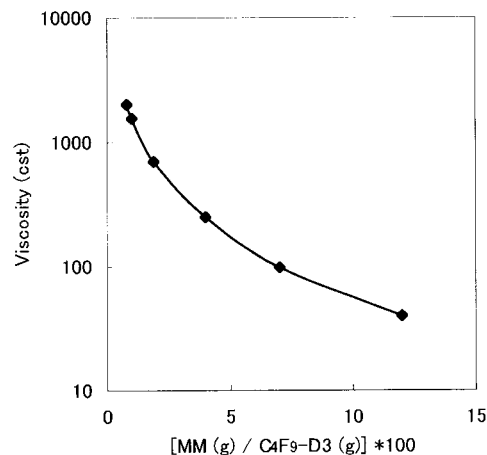

Figure 2 The relationship between the viscosity of the polymer and the amount of MM.

with sodium hydroxide as an alkaline catalyst and the ratio of CF_3–D3/NaOH (mol/mol) is about 5000.[6] When C_4F_9–D3 was subjected to the polymerization under the same conditions, the complete consumption of C_4F_9–D3 was observed by gas chromatography; however, no polymer was obtained, in contrast to the polymerization for CF_3–D3. The analysis of the reaction mixture by gas chromatography showed that 1,3,5,7-tetrakis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane $\{[C_4F_9CH_2CH_2(CH_3)SiO]_4 \ (C_4F_9$–D4)$\}$ was formed as the major product (74.3%). This suggests that the longer fluoroalkyl substituent is attached to a cyclosiloxane tetramer, the more thermodynamically stable it is and the depolymerization occurs via a backbiting mechanism to give the thermodynamically stable C_4F_9–D4. Therefore, it was more important to polymerize C_4F_9–D3 under kinetic control and to termi-

Table I Molecular Weight of PNFHMS Polymerized by Trifluoromethanesulfonic Acid

| Run	Viscosity (cst)	Peak No.	Molecular Weight	
			M_w	M_n
1	217	Average	5,000	3,700
2	1098	Average	12,700	5,400
		1	16,200	2,000
		2	2,000	2,000
3	9000	Average	20,100	4,500
		1	32,900	32,000
		2	2,100	2,100
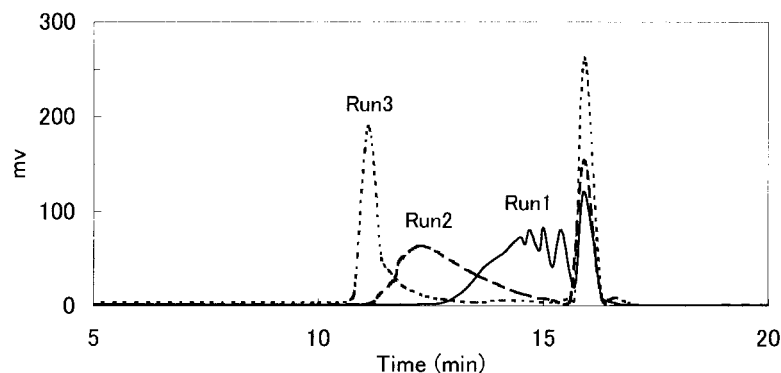
Figure 3 Distribution of molecular weight of PNFHMS polymerized by trifluoromethanesulfonic acid.

nate the reaction before the equilibrium was reached than it was in the case of the polymerization of CF_3–D3. When the polymerization of C_4F_9–D3 was conducted at a lower temperature, an increase in the viscosity was observed. Our best experimental conditions to obtain the polymer with high molecular weight was to polymerize C_4F_9–D3 in the temperature range 0–20°C in the presence of the catalytic amount of KOH activated by the phase-transfer catalysts such as a crown ether or $[(n\text{-Bu})_4N^+Cl^-]$. Actually, we obtained PNFHMS with the viscosity of 10,000,000 cps, but it was associated with the immediate decrease in viscosity and the reproducibility was poor.
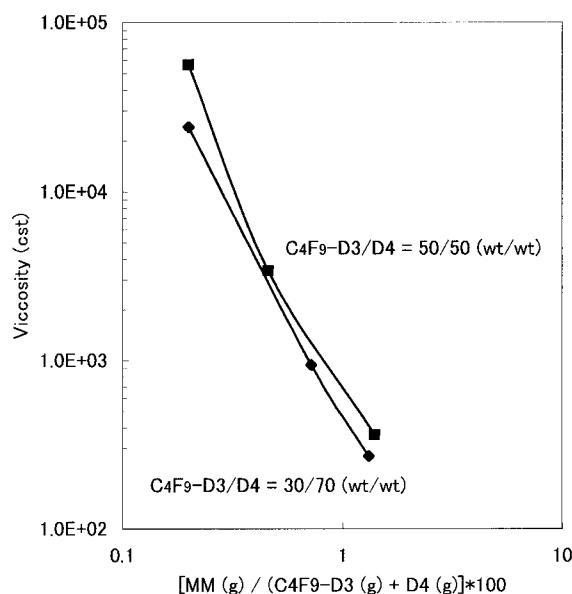
Polymerization of C_4F_9–D3 with an Acid Catalyst

Pierce et al.[7] reported that special catalysts of the type of perfluoroalkanesulfonic acids are required for the polymerization of a fluorinated cyclotrisiloxane. On the basis of this, we studied the polymerization of C_4F_9–D3 using trifluoromethanesu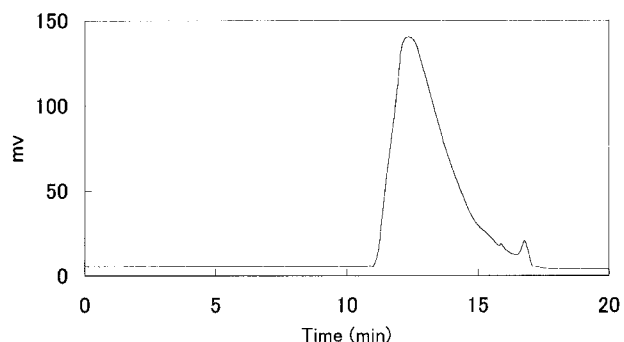lfonic acid as a catalyst. When trifluoromethanesulfonic acid was applied to the polymerization for C_4F_9–D3, the polymerization could be initiated, even at room temperature, and completed within 24 h. A plot of the rate of polymerization versus the catalytic concentrations at 50°C gave an approximately linear relationship with a slope of about 1.8 (Fig. 1). The dependence of the rate of the polymerization on the catalytic concentration for D3 and D4 was reported to be about 2 and the polymerization mechanism of D3 and D4 was suggested to be cationic polymerization.[8] Combining our results showed that the polymerization of C_4F_9–D3 proceeds in a mechanism similar to that of D3 and D4. In contrast to the polymerization of C_4F_9–D3 by the alkaline catalyst, the decrease of viscosity was not observed, even though the polymer was allowed to stand for at
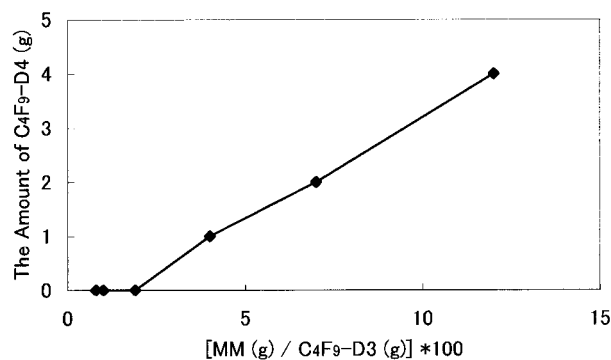
Figure 4 The relationship between the amount of C_4F_9–D4 and the amount of MM.

Figure 5 The copolymerization of C_4F_9–D3 and D4.

Figure 6 Molecular weight distribution of the copolymer between C_4F_9–D3 and D4.

least 24 h at 50°C in the presence of trifluoromethanesulfonic acid catalyst. The viscosity of the polymer was controlled by the amount of hexamethyldisiloxane as the end blocker. The reproducibility of the method was good (Fig. 2). The analysis of the polymers by GPC showed that polymers with bimodal distribution were obtained (Table I, Fig. 3). When the amount of the hexamethyldisiloxane was increased to obtain a polymer with low molecular weight, the increase in the formation of C_4F_9–D4 was observed (Fig. 4). C_4F_9–D4 formed at the initial period of the reaction and once C_4F_9–D4 formed, it remained unchanged during the reaction period. C_4F_9–D4 was inert toward trifluoromethanesulfonic acid, even if the temperature was raised to 100°C. These observations show that the polymerization of C_4F_9–D3 having a longer perfluoroalkyl side chain is apt to form the oligomers including C_4F_9–D4, as in the case of polymerization with sodium hydroxide.

Copolymerization of C_4F_9–D3 with Cyclodimethylsiloxanes

Copolymerizations of C_4F_9–D3 with D3 or D4 were conducted with trifluoromethanesulfonic acid as a catalyst. The reactivity of different methylated polysiloxanes with acid catalysts decreases in the following order and the relative reactivity of D3 and D4 toward acid catalysts is somewhat different.[9]

$$D3 > MM > MDM > MD2M > D4$$

For this reason when two (or more) monomers are allowed to undergo copolymerization to give their copolymer, one cyclotrisiloxane is copolymerized with another cyclotrisiloxane and one cyclotetrasiloxane with another cyclotetrasiloxane to adjust their polymerization rate. However, when the fluorine-containing groups were attached to silicons of cyclosiloxane, the reactivity of the cyclosiloxane toward trifluoromethanesulfonic acid was found to decrease as follows:
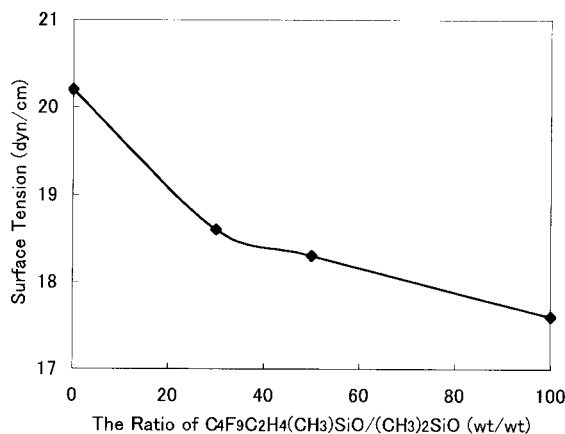
$$D3 > D4 > C_4F_9-D3$$
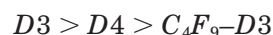
The ratios of their polymerization rate for 10% conversion of each monomer were as follows:

$$D3 : D4 : C_4F_9-D3 = 120 : 5 : 1$$
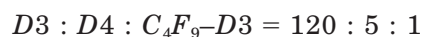
Thus, the reactivity of cyclosiloxanes with trifluoromethanesulfonic acid greatly changed by the substituents on the silicons and, in terms of the polymerization rate, D4 was the more suitable

Table II   Properties of Fluorosilicone Polymers Having 3,3,4,4,5,5,6,6,6-Nonafluorohexyl Group

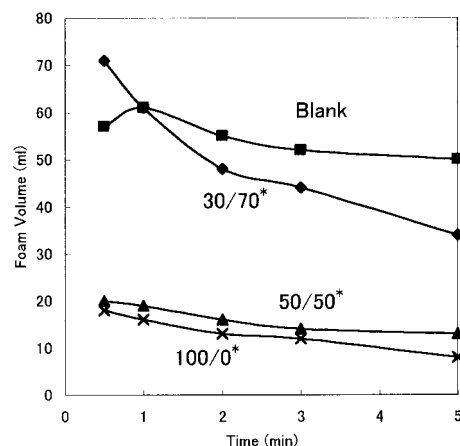|	$C_4F_9C_2H_4(CH_3)SiO/(CH_3)_2SiO$ (wt/wt)			
Property	100/0	50/50	30/70	0/100
Viscosity (cst at 25°C)	250	280	370	300
Specific gravity (at 25°C)	1.52	1.22	1.11	0.97
Surface tension (dyn/cm at 25°C)	17.6	18.3	18.6	20.1
Coefficient of viscosity	0.84	0.73	0.70	0.60
Refractive index (at 25°C)	1.3506	1.3752	1.3855	1.4030
Dielectric constant (at 25°C, 60 Hz)	5.35	4.10	3.50	2.75
Dielectric dissipation factor (at 25°C, 60 Hz)	3.0E-03	6.8E-03	4.7E-04	1.0E-04

Figure 7   Surface tension of the copolymers.

Figure 8   Antifoam test of the toluene foaming system. * = ratio of $[C_4F_9C_2H_4(CH_3)SiO]/[(CH_3)_2SiO]$ (wt/wt).

comonomer for C_4F_9–D3. We selected D4 as a comonomer for C_4F_9–D3 for this reason. The viscosity of the oil was controlled by the amount of MM as the end blocker. The reproducibility of the method was good (Fig. 5). The analysis by GPC showed that the polymer with unimodal distribution was obtained in contrast to the homopolymerization of C_4F_9–D3 (Fig. 6).

## Performance of Fluorosilicone Polymers Having 3,3,4,4,5,5,6,6,6-Nonafluorohexyl Group

The performance of the fluorosilicone polymers having 3,3,4,4,5,5,6,6,6-nonafluorohexyl group was evaluated in terms of the properties shown in Table II. We focused on two kinds of copolymers that have the proportion of $[C_4F_9C_2H_4(CH_3)SiO]/[(CH_3)_2SiO] = 50/50$ and $30/70$ (wt/wt). These properties changed almost linearly with an amount of $[C_4F_9C_2H_4(CH_3)SiO]$ introduced, except for the surface tension. The surface tension of copolymer containing more than 50 wt % of $[C_4F_9C_2H_4(CH_3)SiO]$ unit was almost as low as that of the homopolymer of C_4F_9–D3 (Fig. 7). Considering the surface tension as an important factor for applying the material for various applications, this means that the use of the expensive fluorine-containing monomer may be avoided.

To examine this practically, the application to antifoaming agents was studied. The surface tension is one of the important factors that determine the antifoaming efficiency, although there are some other factors including the dispersion and solubility to foaming systems. Antifoaming agents based on dimethylsilicone are effective for aqueous foaming solutions but are often not effec-

tive for organic foaming solutions. This is probably because they are readily soluble in organic foaming solutions. So, we applied the above-mentioned fluorosilicones to toluene and tetrachloroethylene foaming systems (Figs. 8 and 9, respectively). The copolymer containing 50 wt % of $[C_4F_9C_2H_4(CH_3)SiO]$ unit was as effective as the homopolymer for the toluene system. Thus, it was confirmed that the limited fluorine content demonstrated an antifoam effect. The copolymer containing 30 wt % of $[C_4F_9C_2H_4(CH_3)SiO]$ was not effective as an antifoaming agent.
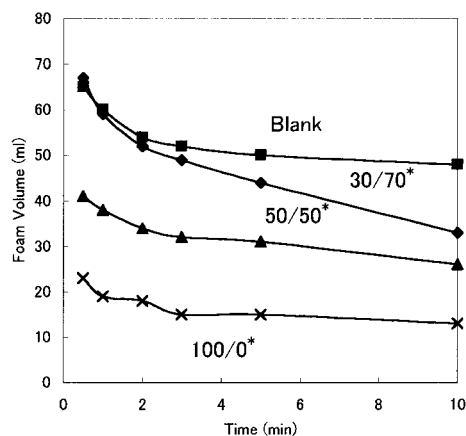
Figure 9   Antifoam test of the tetrachloroethylene foaming system. * = ratio of $[C_4F_9C_2H_4(CH_3)SiO]/[(CH_3)_2SiO]$ (wt/wt).

CONCLUSIONS

The polymerization of C_4F_9–D3 with sodium hydroxide did not yield a high molecular weight polymer in contrast to that of the commercially available CF_3–D3. The major product was C_4F_9–D4.

On the other hand, the polymerization of C_4F_9–D3 with trifluoromethanesulfonic acid proceeded similar to that of CF_3–D3. C_4F_9–D3 was also successfully copolymerized with octamethylcyclotetrasiloxane (D4). The properties of the obtained copolymers changed almost linearly with an amount of $[C_4F_9C_2H_4(CH_3)SiO]$ units, except for the surface tension. The surface tension of the copolymer containing more than 50% $[C_4F_9C_2H_4(CH_3)SiO]$ units by weight was almost as low as that of the homopolymer. When the copolymer containing 50% $[C_4F_9C_2H_4(CH_3)SiO]$ units by weight was examined for an antifoaming agent, it worked as effectively as the homopolymer in the toluene foaming system.

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