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Antifoaming Effects in a Nonaqueous Solvent by Novel Fluorosilicone Oligomers

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It is widely known that organosilicones, consisting of siloxane skeleton $\{-(\text{SiO})_n-\}$ and functional alkyl groups attached as side chains, show excellent antifoaming effects in aqueous solutions^{1)~3)}. However, in nonaqueous (organic) solvents having low surface tension the performance of antifoaming is ineffective as a result of their high solubilities^{4),5)}. Therefore, the introduction of oleophobic fluoroalkyl groups to organosilicones has been of great interest in recent years^{4),5)}. We have previously reported that small amounts of novel fluorosilicone oligomers added to liquid paraffin lower the friction coefficient⁶⁾. The results suggested that the solubility of organosilicones in nonaqueous solvents was substantially reduced by the fluorooxaalkyl group (R_F) as a side chain. In this paper, the novel fluorosilicone oligomers were applied as antifoaming agents in a nonaqueous solution (fluorinated polymer alcohol solution).

The fluorosilicone oligomers used in this experiment were synthesized with vinyl-group-containing poly(dimethylsiloxane)s {VPSs : siloxane chain lengths (n) are 10, 21, 63} and bis(fluorooxaalkanoyl) peroxides $\{R_F=\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7, \text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7\}$ as shown in **Scheme 1**. The synthetic method and preparation of the fluorosilicones were the same in previous studies^{7)~9)}. A typical procedure is as follows. Perfluoro-2, 5-dimethyl-3, 6-dioxanonanoyl peroxide {4.95 g (5 mmol)} in 1, 1, 2-trifluoro-1, 2, 2-trichloroethane (85 g) was added to a mixture of vinyl-group-containing poly(dimethylsiloxane) $\{\text{CH}_2=\text{CH}-\text{SiMe}[(\text{OSiMe}_2)_n\text{OSiMe}_3]_2$; VPS, 17.9 g (10 mmol); $M_n=1790$ ($M_w/M_n=1.27$) and 1, 1, 2-trifluoro-1, 2, 2-trichloroethane (50 g). The solution was stirred for 5 h at 40°C in a nitrogen atmosphere. The solution was then concentrated by evaporating the solvent under reduced pressure. The liquid product obtained was dried in vacuo to yield a colorless fluorosilicone oligomer (22.4 g). This oligomer exhibited the following spectra data. IR (cm^{-1}): 1334 (FC_3), 1242 (CF_2), 799 (Si-Me); $^1\text{H-NMR}$ ($\text{CF}_2\text{ClCFCl}_2$): δ 0.02~0.35 (Si- CH_3), δ 0.66~2.87 ($-\text{CH}_2-$, $=\text{CH}-$). The average molar mass $\{M_n(M_w/$

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M_n)} was determined by gel permeation chromatography (GPC) calibrated with standard polystyrenes. Similarly, the other fluorosilicone oligomers were prepared according to the method mentioned above. The products obtained were polydispersant mixtures of oligomers ($M_w/M_n > 1$) as shown in **Table 1**. The bubbling liquid was prepared by diluting a fluorinated polymer (MODIPER F-200, reagent grade from Nippon Oil & Fats Co.) with 2-propanol to the total concentration of 5 wt%. A small amount (less than 0.5 wt%) of organosilicones (VPSs and/or fluorinated VPSs) was added to the bubbling liquid

Scheme 1 Fluorooxaalkylation of vinyl group-containing poly(dimethylsiloxane)s with bis(fluorooxaalkanoyl) peroxides

Table 1 Fluorooxaalkylation of vinyl group-containing poly(dimethylsiloxane)s with bis(fluorooxaalkanoyl) peroxides

Substrate					Product		
$\text{R}_\text{F}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{R}_\text{F}$		$\begin{array}{c} \text{CH}_2=\text{CH} \\ \diagdown \\ \text{Me}-\text{Si}-(\text{OSiMe}_2)_n-\text{OSiMe}_3 \\ \diagup \\ (\text{OSiMe}_2)_n-\text{OSiMe}_3 \end{array}$			$\begin{array}{c} \text{R}_\text{F}-(\text{CH}_2-\text{CH})_m-\text{R}_\text{F} \\ \diagdown \\ \text{Me}-\text{Si}-(\text{OSiMe}_2)_n-\text{OSiMe}_3 \\ \diagup \\ (\text{OSiMe}_2)_n-\text{OSiMe}_3 \end{array}$		
R_F in $(\text{R}_\text{F}\text{CO}_2)_2$	[mmol]	(g)	M_n	M_w/M_n	Yield (%)	M_n	M_w/M_n
CFOCF_3F_7	5	30.0	9600	(1.12)	94	17500	(2.11)
$\begin{array}{c} \text{CF}_3 \\ \\ \text{CFOCF}_2\text{CFOCF}_3\text{F}_7 \\ \quad \\ \text{CF}_3 \quad \text{CF}_3 \end{array}$	5	30.0	9600	(1.12)	95	24400	(2.84)
$\begin{array}{c} \text{CF}_3 \\ \\ \text{CFOCF}_3\text{F}_7 \\ \\ \text{CF}_3 \end{array}$	4	24.5	3400	(1.34)	98	4400	(1.75)
$\begin{array}{c} \text{CF}_3 \\ \\ \text{CFOCF}_2\text{CFOCF}_3\text{F}_7 \\ \quad \\ \text{CF}_3 \quad \text{CF}_3 \end{array}$	4	24.5	3400	(1.34)	97	14200	(3.06)
$\begin{array}{c} \text{CF}_3 \\ \\ \text{CFOCF}_2\text{CFOCF}_3\text{F}_7 \\ \quad \\ \text{CF}_3 \quad \text{CF}_3 \end{array}$	5	17.9	1790	(1.27)	98	3400	(1.54)

(10 ml) ; then the mixture was shaken 50 times in the test tube at 25°C. The foam ability was evaluated from foam volume after 30 s.

Figure 1 shows the foam ability as a function of organosilicone concentrations {VPS and/or improved (fluorinated) VPS : $R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ }. Both siloxane chain lengths (n) in the organosilicones are $n=10$. The foam ability was almost independent of organosilicone concentrations. No effect of the fluorooxaalkyl group on the reduction of the foam ability was observed.

In the case of a siloxane chain length (n) equal to 21 (**Figure 2**), the foam ability of an unmodified VPS was almost constant in the 2-propanol solutions. It should be noted that improved VPSs showed remarkable antifoaming effects: the foam ability became near zero. The antifoaming effects did not depend on the fluorooxaalkyl chain lengths in the fluorosilicone oligomers but on the concentrations of oligomers.

In the case of a siloxane chain length (n) equal to 63 (**Figure 3**), un-improved VPS was not able to inhibit foaming caused by fluorinated polymer in the 2-propanol solutions, while improved VPSs, which are novel fluorosilicone oligomers, did quite well. The antifoaming effects were almost independent of the fluorooxaalkyl chain lengths in the fluorosilicone oligomers, but fairly dependent of their concentrations.

The effect of the siloxane chain lengths ($n=10, 21, 63$) in the improved VPSs on the foam ability is shown in **Figure 4**. In the case of improved VPS having a short siloxane chain ($n=10$), the foam ability decreased slightly with increasing concentration. However, the addition of a small amount of improved VPS having a longer siloxane chain ($n=21$ and 63) decreased the foam ability less than approximately 20%. In order to elucidate the antifoaming effects (reduction of foam ability), we tried to undergo the

Fig.1 The relationship between foam ability and the concentration of organosilicone at 25°C. {siloxane chain length(n)=10}

Fig.2 The relationship between foam ability and the concentration of organosilicone at 25°C. {siloxane chain length(n)=21}

Fig. 3 The relationship between foam ability and the concentration of organosilicone at 25°C. [siloxane chain length(n)=63]

Fig. 4 The effect of siloxane chain length in the fluorosilicone oligomers on foam ability at 25°C.

static and dynamic surface tension measurements of those sample in 2-propanol solutions similar to previous studies^{10), 11)}. As a result, no effect of the fluoroalkyl group on the reduction of the static and dynamic surface tensions was observed; that is, both the equilibrium surface tension and the dynamic surface tension were independent of organosilicone concentrations. Although there is not enough data in the results to discuss the antifoaming effects of fluorosilicone oligomers, one could suggest that an important factor for the depression of foaming in nonaqueous solution systems is the balance of oleophilic siloxane chain and oleophobic fluoroalkyl group in the fluorosilicone oligomer. Further studies will follow to explain these phenomena in detail.

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