

## Preparation of Poly[(*N*-acetylimino)ethylene] Having (Perfluoroacylimino)ethyl End Group and Its Surface Activity

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**ABSTRACT:** A series of fluorine-containing oligomeric nonionic surfactants consisting of a perfluoroacyl group as the hydrophobic group and poly[(*N*-acetylimino)ethylene] as the hydrophilic group was prepared by the cationic ring-opening oligomerization of 2-methyl-2-oxazoline initiated by a 1:1 adduct of 2-(perfluoroalkyl)-2-oxazoline with methyl trifluoromethanesulfonate or *p*-toluenesulfonate. The degree of polymerization of the obtained oligomers was in a range of 1—7. The superior property of these fluorine-containing nonionic surfactants was demonstrated by the measurement of surface tension of their aqueous solutions.

**KEY WORDS** Nonionic Surfactant / Poly[(*N*-acylimino)ethylene] / Cationic Ring-Opening Polymerization / 2-Methyl-2-oxazoline / 2-(Perfluoroalkyl)-2-oxazolinium Triflate / Surface Tension /

Poly(oxyethylene) derivatives are widely used as nonionic surfactants for various purposes.<sup>1</sup> Recently, another group of polymeric nonionic surfactant has been reported which has poly[(*N*-acylimino)ethylene] (PAE) as the hydrophilic component. The excellent hydrophilicity of PAE has been demonstrated in previous studies where the acyl group is acetyl or propionyl.<sup>2-7</sup>

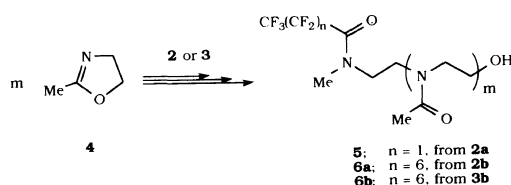
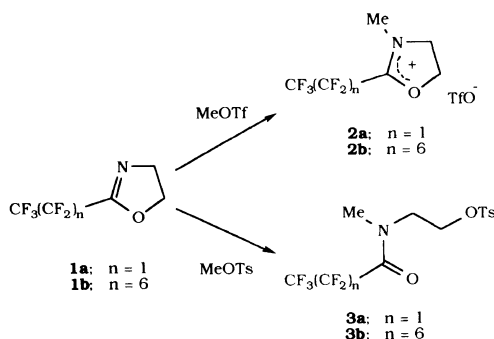
A surfactant having a perfluoroalkyl group as its hydrophobic component is generally known to possess an excellent ability to reduce surface tension. It was already reported that copolymers consisting of two PAE blocks, *i.e.*, poly[(*N*-acetylimino)ethylene] and poly[(*N*-

pentafluoropropanoylimino)ethylene] blocks, were nonionic surfactants of high performance: the values of surface tension of their 0.1 wt% aqueous solutions were 13~32 dyn cm<sup>-1</sup> at 20°C depending on their fluorine content.<sup>5</sup> The preparation of poly[(*N*-acetylimino)ethylene] having a perfluoroacyl terminal group has been also reported.<sup>3,6,7</sup> In these reports (perfluoroacyl)ethyl iodide, tosylate, and triflate were employed as the initiator for the polymerization of 2-methyl-2-oxazoline (**4**) or the living propagating end of PAE was terminated with a non-polymerizable oxazoline having a perfluoroacyl substituent. However, the surface activity of the polymers prepared with

(perfluorooctyl)ethyl triflate as well as that of the polymers by the terminator method were not sufficient as the fluorine containing ones.<sup>3,6</sup> On the other hand, (perfluorooctyl)ethyl iodide and tosylate were not adequate as initiators for the polymerization of **4** since they were not strong enough to control the chain length of PAE due to the electron withdrawing effect of perfluoroalkyl group, which considerably reduces the electrophilicity of these compounds, although the ability of surface tension reduction of the resulting products was satisfactorily high.<sup>7</sup>

Our previous work revealed that the 1 : 1 adduct of 2-(perfluoroethyl)-2-oxazoline (**1a**) with methyl trifluoromethanesulfonate (triflate) (MeOTf) was an ionic compound, 3-methyl-2-(pentafluoroethyl)-2-oxazolinium triflate (**2a**), while that with methyl *p*-toluenesulfonate (MeOTs) was a covalent one, *N*-methyl-*N*-[2-(*p*-toluenesulfonyloxy)ethyl]pentafluoropropanamide (**3a**) (Scheme 1).<sup>8</sup> These compounds are highly electrophilic and are available as the initiator for the polymerization of cyclic imino ethers.

In the present paper similar 1 : 1 compounds



having perfluoroheptyl groups, *i.e.*, 3-methyl-2-(perfluoroheptyl)-2-oxazolinium triflate (**2b**) and *N*-methyl-*N*-[2-(*p*-toluenesulfonyloxy)ethyl]perfluorooctanamide (**3b**), were prepared from 2-(perfluoroheptyl)-2-oxazoline (**1b**) and were employed as the initiator for the polymerization of **4** (Scheme 2). The polymerization of **4** with **2a** was also investigated to compare the difference in the surface activity between the polymers with different perfluoroalkyl chain lengths. The surfactant properties of the resulting oligomers were investigated and discussed in comparison with those prepared in earlier studies.

## EXPERIMENTAL

### Measurements

<sup>1</sup>H NMR spectra were recorded on a 60 MHz Hitachi R-600 or a 400 MHz JEOL JNM-GX400 NMR spectrometer. <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on a Hitachi R-900 NMR spectrometer (22.6 and 84.7 MHz, respectively). IR spectra were obtained on a Hitachi 260-20 infrared spectrometer. Mass spectra were measured with a JEOL MS-DX 300. The GPC measurements were performed by using a TSK-GEL G2500H<sub>XL</sub> column in DMF containing 0.4% triethylamine at 50°C. The number average molecular weight of the sample was also measured by a vapor pressure osmometer (Hitachi Model 114) in acetonitrile at 40°C.

The surface tension of aqueous solutions of surfactants was measured at 20°C by a Wilhelmy-type tensiometer, Kyowa CBVP surface tensiometer A 1, with varying concentration from 1 to 0.001 wt% by dilution. The size of Wilhelmy glass plates was 24.0 × 24.0 × 0.3 (mm). The equilibrium surface tension was obtained from the extrapolation of the time-dependent values of surface tension according to the equation reported by Bartholomé and Schäfer.<sup>9</sup>

### Materials

2-(Perfluoroethyl)-2-oxazoline (**1a**) and 2-(perfluoroheptyl)-2-oxazoline (**1b**) were prepared and purified according to a reported procedure.<sup>8</sup> 2-Methyl-2-oxazoline was purchased from Aldrich Co. and was purified by repeated distillations over KOH pellets under nitrogen. The other reagents and the solvents were commercial ones. They were dried by conventional methods and were distilled under nitrogen.

3-Methyl-2-(pentafluoroethyl)-2-oxazolinium triflate (**2a**) was prepared according to the preceding paper.<sup>8</sup> 3-Methyl-2-(perfluoroheptyl)-2-oxazolinium triflate (**2b**) was prepared as white crystals in a similar procedure in 70% yield; mp 111–113°C; <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>) 3.79 (s, CH<sub>3</sub>-N, 3H), 4.78 (t, CH<sub>2</sub>-N, 2H), 5.52 (t, CH<sub>2</sub>-O, 2H); <sup>19</sup>F NMR (CD<sub>3</sub>NO<sub>2</sub>) -46.5 (m, CF<sub>2</sub>CF<sub>3</sub>, 2F), 42.9–41.4 (m, (CF<sub>2</sub>)<sub>4</sub>CF<sub>2</sub>-CF<sub>3</sub>, 8F), -34.9 (t, COCF<sub>2</sub>, 2F), -2.1 (t, CF<sub>3</sub>, 3F).

*N*-Methyl-*N*-[2-(*p*-toluenesulfonyloxy)-ethyl]perfluorooctanamide (**3b**) was prepared by the reaction of **1b** with two-fold excess amounts of MeOTf at 110°C for 3 days. The product was isolated by distillation under a reduced pressure and was purified by reprecipitation from chloroform (solvent) to hexane (non-solvent). The yield was 71%. **3b** was a mixture of two interconvertible isomers **3b-s** (syn) and **3b-a** (anti) whose ratio was 83:17 in CDCl<sub>3</sub> at 35°C. **3b**: mp 70–71°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 2.35 (s, CH<sub>3</sub>-Ph, 3H), 3.24 (s, CH<sub>3</sub>-N, 3H), 3.2–3.8 (brs, CH<sub>2</sub>, 4H), 6.90–7.90 (m, aromatic protons, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 21.3 (CH<sub>3</sub>Ph), 36.2 (CH<sub>3</sub>N of **3b-a**), 37.1 (CH<sub>3</sub>N of **3b-s**), 48.1 (CH<sub>2</sub>N of **3b-a**), 47.9 (CH<sub>2</sub>N of **3b-s**), 67.1 (CH<sub>2</sub>-O), 89.5–124.2 (CF<sub>2</sub> and CF<sub>3</sub>), 127.8, 130.0 (2 and 3-positions of phenyl group), 132.4 (4-position of phenyl group), 145.4 (1-position of phenyl group), 156.8–159.1 (C=O); <sup>19</sup>F NMR (CD<sub>3</sub>NO<sub>2</sub>) -47.0 (m, CF<sub>2</sub>CF<sub>3</sub>), -44.1–-40.8 (m, (CF<sub>2</sub>)<sub>4</sub>CF<sub>2</sub>CF<sub>3</sub>), -33.1 (t, CF<sub>2</sub>CO of **3b-s**), -31.4 (CF<sub>2</sub>CO of **3b-a**), -1.7 (s, CF<sub>3</sub>); IR

(KBr) 3050 (ν<sub>C-H</sub>), 2950 (ν<sub>C-H</sub>), 1680 (ν<sub>C=O</sub>), 1360 (ν<sub>S=O</sub>), 1260–1110 (ν<sub>C-F</sub>) cm<sup>-1</sup>.

### Preparation of Oligo[(*N*-acylimino)ethylene] Having Perfluoroalkyl End Group

A typical run was as follows. In a test tube equipped with a magnetic stirrer bar and a three-way stopcock were mixed 0.432 g (0.714 mmol) of **1b**, 0.304 g (3.57 mmol) of **4**, and 2 mL of nitromethane under cooling at -78°C. The tube was sealed and kept at 70°C for 20 h. Then, the reaction mixture was dried *in vacuo*, and the resulting crude oligomer was dissolved in methanol. The solution was treated with Amberlite IRA-410 of OH form for two hours with stirring to hydrolyze the oxazolinium ion at the propagating end of the polymer and to remove the tosylate anion. After removing the ion-exchange resin by filtration, the product was isolated by reprecipitation to an equivolume mixture of diethyl ether with hexane.

## RESULTS AND DISCUSSION

### Preparation of 5 and 6

The 1:1 adducts of **1b** with MeOTf and with MeOTs were prepared according to similar procedures as those for **2a** and **3a**, respectively, and spectroscopic evidences showed that the adduct with MeOTf was an ionic compound, **2b**, while that with MeOTs was a covalent one, **3b**, as expected from the structure of their 2-pentafluoroethyl homologues (see the EXPERIMENTAL section).

The oligomerization of **4** with these adducts was carried out in nitromethane at 70 or 80°C. The molar ratios of monomer to initiator were set to 1–5 in these runs to examine the effect of chain length of the hydrophilic poly[(*N*-acetylimino)ethylene] moiety on the surfactant property.

The resulting oligomers were treated with Amberlite IRA-410 of OH form to convert the oxazolinium terminal end to the hydroxyethyl group to avoid the influence of terminal ionic

**Table I.** Preparation of nonionic surfactant by the polymerization of **4**<sup>a</sup>

Initiator	$\frac{[M]}{[I]}$	Temp.	5 or 6	Product polymer			
		°C		Yield/wt%	$M_n^b$	$M_n^c$	$DP^c$
<b>2a</b>	1.1	70	<b>5-1</b>	25	400	300	1.0
<b>2a</b>	2.1	70	<b>5-2</b>	38	510	430	2.4
<b>2a</b>	3.1	70	<b>5-3</b>	55	580	460	2.8
<b>2b</b>	1.0	70	<b>6a-1</b>	23	800	560	1.0
<b>2b</b>	1.4	70	<b>6a-2</b>	41	730	630	1.9
<b>2b</b>	2.0	70	<b>6a-3</b>	46	740	660	2.2
<b>2b</b>	3.3	70	<b>6a-4</b>	69	840	750	3.3
<b>2b</b>	4.3	70	<b>6a-5</b>	74	838	870	4.7
<b>2b</b>	5.4	70	<b>6a-6</b>	81	1000	1010	6.3
<b>3b</b>	1.0	80	<b>6b-1</b>	28	820	720	2.9
<b>3b</b>	2.0	80	<b>6b-2</b>	61	840	870	4.7
<b>3b</b>	3.0	80	<b>6b-3</b>	51	840	890	4.9
<b>3b</b>	5.0	80	<b>6b-4</b>	72	1130	1050	6.8

<sup>a</sup> Solvent; nitromethane, reaction time; 20 h. The resulting polymers were treated with ion-exchange resin to remove the terminal sulfonate group. <sup>b</sup> Determined by VPO in chloroform at 35°C. <sup>c</sup> Determined from the integral ratio of the peaks ascribed to  $NCH_2$  and  $C(O)CH_3$  in the  $^1H$  NMR spectrum on the assumption that each polymer molecule has one initiator derived group.

group on the surface activity. The alkaline hydrolysis of oxazolinium terminal groups of polymers has already been carried out by the treatment with aqueous  $Na_2CO_3$  or NaOH in MeOH.<sup>10,11</sup> But, we employed the ion exchange resin because of the easiness of workup.

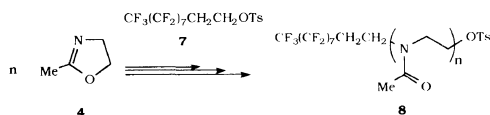
The completion of hydrolysis was confirmed from the absence of the sulfonate group as well as the absence of the amino ester, which is the other possible product of hydrolysis of the oxazolinium ion, by  $^1H$  NMR and IR spectroscopies.

The results of the oligomerization of **4** with these adducts as well as with **2a** are summarized in Table I. The yields were those after the alkaline treatment. The consumption of monomer was almost complete in the every case. However, the polymer yields were relatively low, especially in the cases with low  $[M]/[I]$  ratios, due to the loss in the purification process as well as the presence of the unreacted initiator in the cases using **3b**. The degree of polymerization generally coincided well with the feed ratio when **2a** or **2b** was employed as the initiator, while it tended to overcome the

feed ratio in the cases with **3b**, indicating a lower initiating efficiency of **3** in comparison with **2**.

The lower reactivity of **3** was already demonstrated from the results of the equimolar reactions of **2a** and **3a** with **4** in the preceding paper.<sup>8</sup> The reaction of **2a** with **4** was very rapid at 35°C in nitromethane- $d_3$  and the perfect conversions of the both were attained within 1 min, which indicated that the initiation exclusively occurs without accompanying the propagation. On the other hand, the covalent species **3a** was more stable and the initiation and propagation of **4** concurrently proceeded at 60°C: the conversions of **3a** and **4** after 30 min were 57% and 85%, respectively.

Although the precise control of the PAE chain length could not be achieved when **3b** was used as the initiator, **3b** gave still better results than the case of 2-(perfluorooctyl)ethyl tosylate **7**: the equimolar reaction of **7** with **4** yielded an oligomer **8** whose DP was 6.2 (Scheme 3).<sup>7</sup>



### Surface Activity of Oligomers

Thus obtained oligomers **5** and **6** consisting of the hydrophobic perfluoroalkyl group and the hydrophilic PAE chain whose degree of polymerization (DP) were in the range of 1–6.8. Their surface activity was evaluated by surface tension of their aqueous solutions.

Figure 1 shows a plot of surface tension of aqueous solutions of **6a** versus their concentration in logarithm.

Critical micelle concentrations (cmc) of the samples are given by inflection points of the curves. Obviously, the PAE chain length strongly influenced on the surface tension of the samples: the curves move upward and, simultaneously, right as increasing the PAE chain length. As the result, the both cmc and the value of surface tension at cmc ( $\gamma_{cmc}$ ) increased as the increase of chain length, which are shown in Figure 3.

Similar linear relationships were already observed in the studies on nonionic surfactants containing a poly(oxyethylene) block as the hydrophilic moiety, and the following explanation has widely been accepted, which is also applicable to the present study.<sup>12,13</sup> As the increment of DP of hydrophilic block the surfactant becomes more soluble in an aqueous medium and, at the same time, its molecular area in the adsorbed surface film increases, which causes the decrease of the density of hydrophobic group at the surface. The former causes the increase of cmc and the latter causes the increase of surface tension.

The other series of **6**, **6b**, has the same structure as **6a** and, therefore, also indicated an excellent ability for the surface tension reduction (see Figure 2). However, the activity of **6b** was not the same as that of **6a**. The curves shown in Figure 2 are not horizontal above

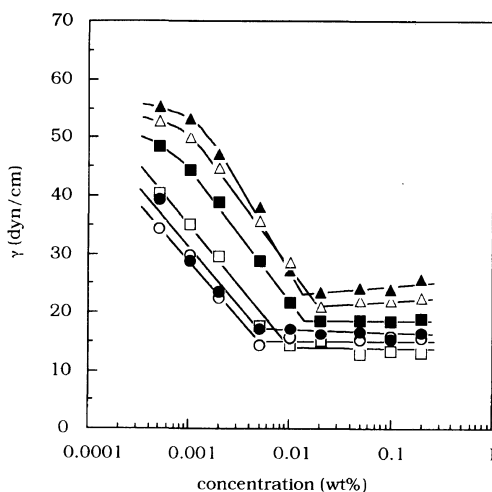


Figure 1. Surface tension curves for the series of **6a** at 20°C. ○, **6a-1**; ●, **6a-2**; □, **6a-3**; ■, **6a-4**; △, **6a-5**; ▲, **6a-6**.

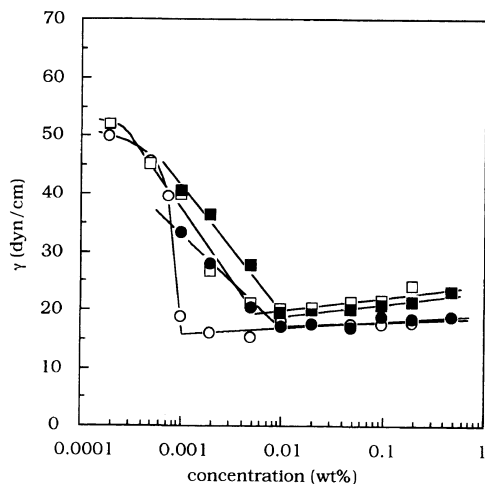
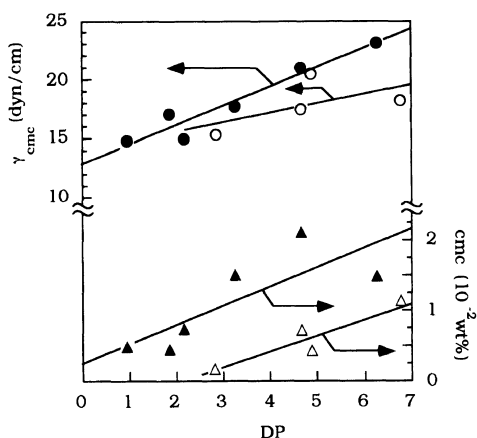


Figure 2. Surface tension curves for the series of **6b** at 20°C. ○, **6b-1**; ●, **6b-2**; □, **6b-3**; ■, **6b-4**.

their cmc as in the case of **6a**, but increase slightly as increasing the concentration.

Although linear relationships between the chain length and the cmc and between the DP and the  $\gamma_{cmc}$  were also observed in this series as indicated Figure 3, the both cmc and  $\gamma_{cmc}$  values for **6b** were generally lower than those for **6a** with a similar DP.

This discrepancy is attributed to the higher

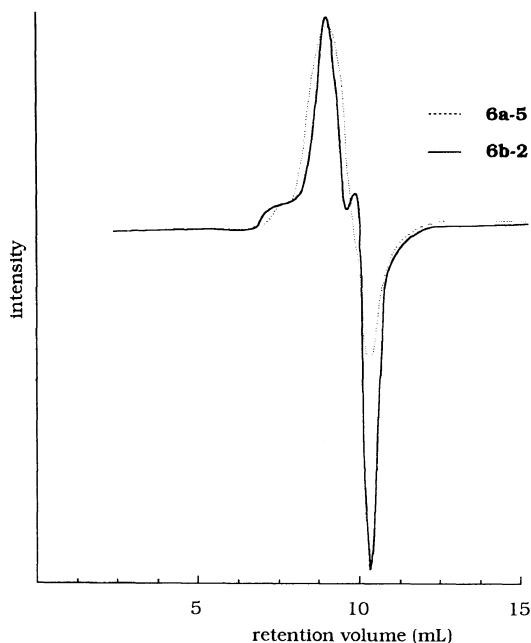


**Figure 3.** Relationship between DP and  $cmc$  or  $\gamma_{cmc}$  in the series of **6**. ● and ▲, **6a**; ○ and △, **6b**.

content of a low DP fraction in **6b** than in the **6a** sample with a similar number average molecular weight. It is highly suspected that the molecular weight distribution of **6b** will be broader than that of **6a**, although the GPC measurements of **6** did not give reliable values since their refractive index strongly depended on the chain length of PAE.

Figure 4 shows the GPC curves for **6a-5** and **6b-2** detected by RI. The downward peaks at around 10 ml of retention volume are due to the shortest oligomer ( $DP=1$ ) as far as judging from the calibration curve with polystyrene standards. Although the number average molecular weights of these samples determined by NMR were the same, Figure 4 shows the content of the shortest oligomer is greater in **6b-2** than in **6a-5**.

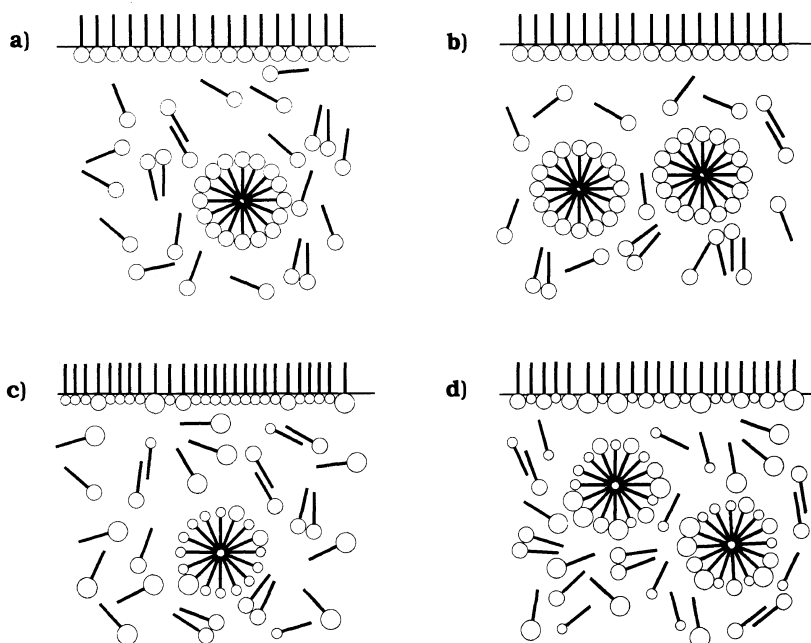
The surfactant with a short hydrophilic chain is inherently less water-soluble than the longer one and, therefore, forms micelles at a lower concentration and orders at the surface predominantly. Since the molecular size of **6** with a short hydrophilic chain is smaller than its higher homologue,  $\gamma_{cmc}$  of the sample of wide distribution is lower than that for the mono-dispersed sample even if their average molecular weights are the same. Figure 5 illustrates this discrepancy. When a surfactant of



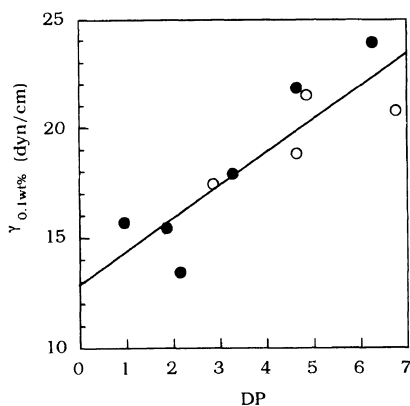
**Figure 4.** GPC curves for **6a-5** and **6b-2** with RI detection.

wide distribution is employed, molecules having a relatively short hydrophilic chain mainly consist micelles and the adsorbed surface film, while more hydrophilic ones remain in water as the solute at the concentration just above  $cmc$  (Figure 5c). Similar phenomena have already found for the samples derived from poly(oxyethylene).<sup>14</sup>

Although significant differences were observed between **6a** and **6b** in their  $cmc$  and  $\gamma_{cmc}$ , their ability for the surface tension reduction at higher concentrations than their  $cmc$  were similar with each other. Figure 6 shows a plot of the values of  $\gamma$  at 0.1 wt% versus the DP. The both data for **6a** and **6b** well satisfied the same linear relationship. This observation is explained with considering model systems illustrated in Figure 5. As the addition of surfactant of wide distribution to the solution above its  $cmc$  (c→d), surfactant molecules having a longer hydrophilic chain become insoluble in the medium and incorporate micelles and the adsorbed surface film,



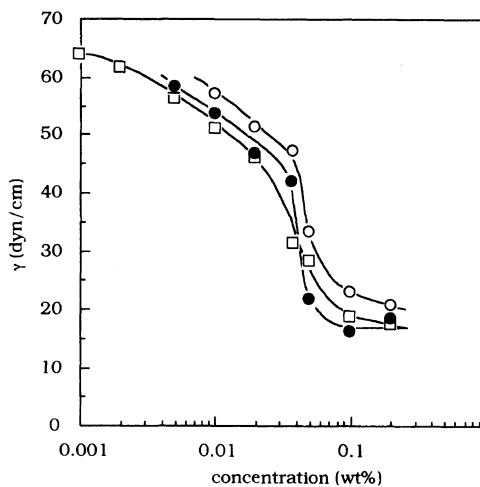
**Figure 5.** Schematic illustration for the arrangements of mono-dispersed and distributed surfactants in aqueous media, whose concentrations are just above their cmc (a, c) and far above their cmc (b, d).



**Figure 6.** Plot of DP versus the surface tension of 0.1 wt% aqueous solutions of **6**. ●, **6a**; ○, **6b**.

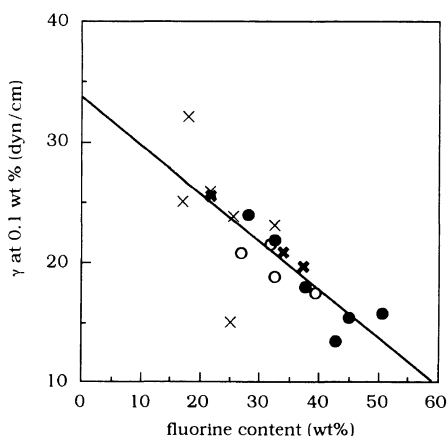
which causes the increase of surface tension. On the other hand, no significant change in the surface tension occurs by the addition of monodispersed surfactant above its cmc (a→b). This observation assists the assumption that **6a** has the relatively narrow molecular weight distribution.

Contrary to **6**, their perfluoroethyl homo-



**Figure 7.** Surface tension curves for the series of **5** at 20°C. ○, **5-1**; ●, **5-2**; □, **5-3**.

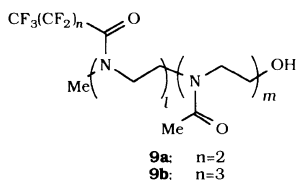
logue **5** showed no clear cmc in aqueous solutions and surface tension curves for **5** were similar to those for ordinary compounds having no surface activity (Figure 7). It is in a good contrast to our previous result that a poly[(*N*-pentafluoropropanoylimino)ethyl-



**Figure 8.** Relationship between the fluorine content of the surfactants and  $\gamma$  at 0.1 wt%. ●, **6a**; ○, **6b**; ×, **9a**, **9b**.

ene]block whose DP were in a range of 3–5 worked well as the hydrophobic group of nonionic surfactant.<sup>5</sup>

In the present and the preceding studies we have shown two different types of surfactant can be prepared from the combination of 2-(perfluoroalkyl)-2-oxazoline and **4**. One has a long perfluoroalkyl chain per molecule and the other has several short perfluoroalkyl groups per molecule. When we compare the surface activity of **6** to that of block copolymers of 2-(perfluoroalkyl)-2-oxazoline with **4** (**9a** from 2-(perfluoroethyl)-2-oxazoline and **9b** from 2-(perfluoropropyl)-2-oxazoline), no significant difference was observed between them: the cmc values were in a similar range and the values of  $\gamma$  at 0.1 wt% were independent of the surfactant structure. But, it depends only on the fluorine content of the surfactant as shown in Figure 8.



The data shown in Figures 1–4 indicate that the surfactants having even one (*N*-acylimino)-ethylene unit showed an excellent surface

activity, while a poly(oxyethylene)-base surfactant requires at least four to five oxyethylene units to reveal surface activity.<sup>1</sup> It is due to the high hydrophilicity of amide in comparison to ether: it is well known that *N,N*-dimethylacetamide, a unit model for PAE, is more polar and hydrophilic than diethyl ether, that for poly(oxyethylene). This will be the most distinguish advantage of the PAE-base nonionic surfactant, since one can design a compact surfactant, which occupies a small area in the adsorbed surface film and forms a highly hydrophobic surface as reported in the present work.

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