(6) Ronca, G.; Russell, T. P. *Phys. Rev. B: Condens. Matter* **1987**, *35*, 8566.
(7) Leibler, L. *Macromolecules*, **1980**, *13*, 1602.
(8) Hadziioannou, G.; Mathis, A.; Skoulios, A. *Colloid Polym. Sci.* **1979**, *257*, 136.
(9) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(10) Fesko, D. G.; Tschoegl, N. W. *J. Polym. Sci.* **1971**, *35*, 51.
(11) Hermans, J. J.; Hermans, P. H.; Vermaas, D.; Weidinger, A. *Recl. Trav. Chim. Pays-Bas* **1946**, *65*, 427.
(12) Kraus, G.; Naylor, F. E.; Rollamnn, K. W. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 1839.
(13) Gouinlock, E. V.; Porter, R. S. *Polym. Eng. Sci.* **1977**, *17*, 535.
(14) Chung, C. I.; Gale, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1149.
(15) Futamura, S.; Meineche, E. A. *Polym. Eng. Sci.* **1977**, *17*, 563.
(16) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(17) Roe, R. J.; Zin, W. C. *Macromolecules* **1980**, *13*, 1221.
(18) Folkes, M. J.; Keller, A.; Scalisi, F. P. *Kolloid Z. Z. Polym.* **1973**, *251*, 1.

Poly[(acylimino)alkylene] Block Copolymers Having Perfluoroalkyl Hydrophobic Blocks: Synthesis and Surfactant Properties

Masatoshi Miyamoto, Keigo Aoi, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan. *Received July 29, 1988; Revised Manuscript Received January 31, 1989*

ABSTRACT: The block cooligomer between 2-(perfluoroalkyl)-2-oxazoline and 2-methyl(or 2-ethyl)-2-oxazoline was prepared by the so-called "one-pot two-stage" polymerization. The copolymer consists of a hydrophobic and a hydrophilic block, which exhibits excellent properties of water-soluble surface active agents. The monomers of the first-stage polymerization were 2-(pentafluoroethyl)-2-oxazoline (**1a**), 2-(heptafluoro-*n*-propyl)-2-oxazoline (**1b**), and 2-(pentafluoroethyl)-5,6-dihydro-4*H*-1,3-oxazine (**2**), and methyl triflate was the initiator. 2-Methyl- (**3a**) and 2-ethyl-2-oxazoline (**3b**) were used in the second-stage polymerization. The surface activity was evaluated by surface tension (γ) of aqueous solutions. The block copolymer showed very low values of critical micelle concentration (cmc) and γ values. The γ value of a sample derived from **1a** and **3a** was as low as 15.0 dyn/cm at 0.1 wt %. It is worthy to note that even short perfluoroalkyl chains (C_2F_5 and C_3F_7 groups) are quite effective in reducing the surface tension value of aqueous solution when these chains are present in the pendant groups of homosequence units of a length (degree of polymerization) longer than 2.7.

Introduction

Hydrophilicity and lipophilicity (hydrophobicity) of cyclic imino ethers have successfully been controlled by changing the substituent at the 2-position of the imino ether ring of the monomer. For example, the polymers of 2-methyl- (**3a**) and 2-ethyl-2-oxazoline (**3b**) are hydrophilic and are easily soluble in water. On the other hand, the polymers of oxazolines having a longer alkyl substituent are hydrophobic.[1] This difference of property among the above polymer homologues has successfully been applied to the preparation of a novel type of nonionic surfactants which were AB- or ABA-type block copolymers between two different cyclic imino ethers, one giving rise to a hydrophobic block and the other to a hydrophilic block.[1,2]

In comparison to the values of ionic surfactants, the surface tension values of nonionic surfactants are influenced by electrolyte to a much less extent.[3] In addition, the critical micelle concentration (cmc) in aqueous solution is lower.

As described in the preceding paper,[4] the ring-opened polymers of 2-perfluoroalkyl-substituted cyclic imino ethers, i.e., 2-(pentafluoroethyl)-2-oxazoline (**1a**), 2-(heptafluoro-*n*-propyl)-2-oxazoline (**1b**), and 2-(pentafluoroethyl)-5,6-dihydro-4*H*-1,3-oxazine (**2**), are very hydrophobic in spite of the short chains of the perfluoroalkyl substituents. The surface energy of **1b** polymer film is similar to the value of poly(1,1-dihydroperfluorooctyl methacrylate), which is taken to be a representative fluorine-containing polymer with a low surface energy.[5]

The present paper describes the synthesis of block copolymers of perfluoroalkyl-substituted cyclic imino ethers with **3** by means of the so-called "one-pot two-stage copolymerization technique" based on the living character of the polymerization of cyclic imino ethers. Namely, a sequential polymerization of two monomers in a single pot of the polymerization system gives rise to the production of an AB-type block copolymer.

Perfluoroalkyl-containing surfactants are generally known to possess an excellent ability to reduce surface tension. However, for nonionic surfactants based on perfluoroalkyl groups, the hydrophilicity of the conventional hydrophilic component of poly(oxyethylene) is not enough to balance with the highly hydrophobic property of the perfluoroalkyl group.[6,7] For example, poly(oxyethylene) (DP = 8) with a perfluorooctyl end group is insoluble in water at room temperature,[6] and higher DPs of the poly(oxyethylene) block are required for water solubility. In the present study, highly hydrophilic oligomers of cyclic imino ethers have been combined with the corresponding oligomers having a perfluoroalkyl group, in order to explore a new type of nonionic surfactant of high performance. It is interesting that short perfluoroalkyl groups (C_2F_5 or C_3F_7 group) are hydrophobic enough to produce excellent surfactants when these groups are present in the homosequence of a block copolymer.

Results and Discussion

The block copolymer was easily prepared by a one-pot two-stage copolymerization of two different types of cyclic imino ethers. First, **1** or **2** was polymerized, and after the completion of the first-stage polymerization the second monomer **3** was added to the reaction mixture. The second-stage polymerization was initiated by the propagating end group of the A block of the first monomer to produce the B block (Scheme I).

As described before,[4] the polymerization of **1** with an alkyl triflate initiator proceeds via a reactive oxazolinium intermediate, whereas the polymerization with alkyl to-

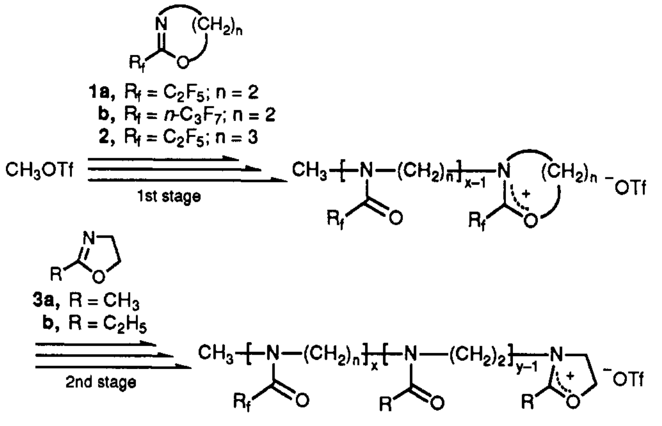
0024-9297/89/2222-3540$01.50/0

Table I
Preparation of Block Copolymers

	1st stage[a]				2nd stage[b]		block copolymers						
										$\bar{M}_w/\bar{M}_n$	unit ratio x:y		
entry	M_1	$[M_1]_0/[I]_0$	temp, °C	time, h	M_2	$[M_2]_0/[I]_0$	polymn	yield, %	$\bar{M}_n$ (VPO[c])	(GPC[e])	VPO	NMR	anal.
1-0	**1a**	3.0	40	25			**4a**	83	550[d]	1.6	2.7:0	3.4:0	
1-1	**1a**	3.0	40	25	**3a**	2.8	**6a**-1	34	1020	1.5	2.7:5.5	3.4:4.0	
1-2	**1a**	3.0	40	25	**3a**	5.0	**6a**-2	57	1170	1.5	2.7:7.3	3.4:8.7	
1-3	**1a**	3.0	40	25	**3a**	9.9	**6a**-3	85	1490	1.5	2.7:11.1	3.4:11.6	
2-0	**1a**	5.0	40	25			**4a**	69		1.3		5.4:0	
2-1	**1a**	5.0	40	25	**3a**	3.2	**6a**-4	60		1.5		5.4:6.8	5.4:6.0
2-2	**1a**	5.0	40	25	**3a**	4.9	**6a**-5	70		1.5		5.4:8.1	5.4:10.9
2-3	**1a**	5.0	40	25	**3a**	10.1	**6a**-6	86		1.6		5.4:15.0	5.4:20.7
3-0	**1b**	3.0	40	25			**4b**	84	710[d]	1.6	2.8:0	3.1:0	
3-1	**1b**	3.0	40	25	**3a**	3.0	**6b**-1	62	1000	1.5	2.8:3.4	3.1:3.2	
3-2	**1b**	3.0	40	25	**3a**	5.0	**6b**-2	71	1090	1.4	2.8:4.4	3.1:6.0	
3-3	**1b**	3.0	40	25	**3a**	9.9	**6b**-3	69	1360	1.4	2.8:7.6	3.1:12.2	
4-0	**1b**	3.0	40	25			**4c**	96	930[d]	1.4	2.9:0	2.8:0	
4-1	**1b**	3.0	40	25	**3b**	3.0	**6c**-1	46	1050[d]	1.4	2.9:3.2	2.8:3.1	2.8:3.5
4-2	**1b**	3.0	40	25	**3b**	5.1	**6c**-2	62	1270[d]	1.4	2.9:5.4	2.8:5.0	2.8:5.8
4-3	**1b**	3.0	40	25	**3b**	9.9	**6c**-3	73	1770[d]	1.3	2.9:10.4	2.8:11.3	2.8:12.4
5-0	**2**	3.0	70	12			**5**	98	580[d]	1.1	2.7:0	3.0:0	
5-1	**2**	3.0	70	12	**3a**	3.0	**7**-1	86	890	1.2	2.7:3.6		3.0:3.9
5-2	**2**	3.0	70	12	**3a**	4.9	**7**-2	92	1020	1.3	2.7:5.2		3.0:6.4
5-3	**2**	3.0	70	12	**3a**	9.9	**7**-3	93	1360	1.3	2.7:9.2		3.0:13.2

[a] In CH_3NO_2. [b] At 70 °C, for 12 h. [c] In $CHCl_3$. [d] In CH_3CN. [e] Measured in DMF at 50 °C. The values were estimated from poly(2-methyl-2-oxazoline) standards.

Scheme I



sylate grows via a covalent-type species of sulfonate ester, which is much less reactive than the corresponding ionic (oxazolinium) propagating species. Therefore, methyl triflate was selected as initiator in the present study.

Table I shows the results of block copolymerization. To investigate the hydrophobic property of the block copolymers, the feed ratio of **1** or **2** to methyl triflate was adjusted to 3.0–5.0 in every run. In these cases the number of fluorine atoms in one molecule of the resulting copolymer was expected to be in the range 15–35 on the assumption of the complete conversion of the monomer, which is quite similar to those in usual surfactants having one long perfluoroalkyl group. In every series of the polymer samples, three polymers of a common length of hydrophobic block with different lengths of hydrophilic blocks were prepared in order to see the effect of the length of the hydrophilic group.

After the complete conversion of the first monomer, which was easily confirmed by ^{19}F NMR spectroscopic measurement, the reaction mixture was divided into four portions. One of these was subjected directly to the workup procedure in order to determine the structure, length, and yield of the resulting homopolymer corresponding to the A block. The other three portions were employed separately to initiate the second-stage polymerization with three different amounts of the second monomer. After the second-stage polymerization, the resulting copolymer was isolated by reprecipitation from 50/50 diethyl ether and hexane. Thus, a series of the copolymers with the same length of A block and different lengths of B block were prepared.

The first-stage polymerization was carried out at 40 °C (for **1**) or at 70 °C (for **2**), and the conversions of monomers to poly[(perfluoroacylimino)ethylene] (**4**) or poly[(perfluoroacylimino)trimethylene] (**5**), respectively, were found by ^{19}F NMR spectroscopy to be almost quantitative. In every case, the molecular weight of the first-stage homopolymer, which was determined by VPO and/or 400-MHz ^1H NMR, was in good agreement with the calculated value from the feed ratio. The less reactive monomer **2** required a higher reaction temperature, but the molecular weight distribution of the resulting first-stage homopolymer, **5**, was quite narrow.

The composition of the block copolymer was determined by three methods, i.e., ^1H NMR, the comparison of molecular weight between the first- and second-stage polymerization products, and elemental analysis. The compositions of copolymers **6** (in Table I), which were derived from **1** and **3a**, were determined by the integral ratio of the ^1H NMR signals due to CH_3 groups of the monomeric units in the B block (δ 2.1) with those of NCH_2 groups (δ 2.9–3.9) in both blocks. This method could not be applied to the block copolymer derived from **2** and **3a** (copolymer **7** in Table I), since the signals of the latter unit were completely overlapped with those of $NCCH_2$ in the A block. The overall copolymer compositions were also calculated on the basis of the molecular weights of the homo- and copolymers. In the series of entries 2-0 to 2-3 in Table I, however, the molecular weight method could not be applied, because the homopolymer of **1a** was not sufficiently soluble in each of the solvents, acetonitrile and chloroform, for VPO measurements. In most cases, the values of the copolymer composition thus determined were in good agreement with each other. In the cases of the experiments with low feed of **3**, especially entry 1-1, a significant difference was observed between these values and the expected one calculated from the feed ratios. Moreover, the yields of the block copolymer increase with increasing the feed ratio of the second monomer to the

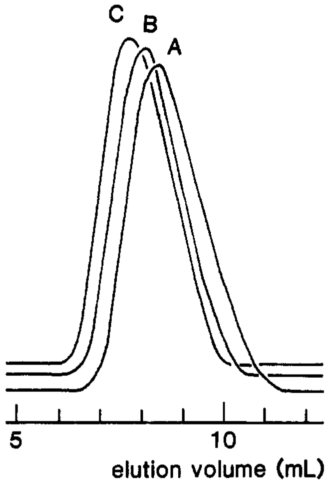


Figure 1. GPC charts of three polymer samples: (A) entry 1-0; (B) entry 1-2; (C) entry 1-3.

initiator. These observations may be explained by a incomplete recovery of block copolymer during reprecipitation, i.e., the loss of block copolymer with relatively short length of B block, which is soluble in the precipitant (equivolume mixture of Et_2O and hexane). In fact, it was found in entry 1-1 that 66% of the block copolymer, whose unit ratio was 2.7:1.3 (by NMR), was recovered when the supernatant layer of precipitation was dried up. In this case, the combined yield of block copolymer amounted to 100%. This finding is taken to show that each step of the polymerization proceeded completely.

The formation of the copolymer was clearly demonstrated by gel permeation chromatography (GPC). All copolymers as well as homopolymers indicated unimodal peaks in their GPC charts. For example, Figure 1 shows GPC curves of two block copolymers (entries 1-2 and 1-3) and of the corresponding homopolymer (entry 1-0). The peak positions shift toward a higher molecular weight region with increasing the length of the B block.

Molecular weight distributions of the copolymers indicated by $\bar{M}_w/\bar{M}_n$ values are in the range 1.3–1.6 for **6** and 1.2–1.3 for **7**. These values are quite close to the value of the corresponding homopolymer of the first-stage polymerization. This finding suggests fast initiation of the second-stage polymerization of monomer **3**, with a highly reactive perfluoroalkyl oxazolinium propagating end.

In addition, the comparison between the molecular weight distributions in the **1**/**3** and **2**/**3** copolymerization systems shows that **2** is a more desirable monomer to achieve uniform composition of the block copolymer. As described above, the unit numbers in the copolymer blocks are governed by the feed molar ratio of monomer to initiator.

Previous studies have clarified that the homopolymers of **1** and **2** showed excellent water and oil repellencies, although their perfluoroalkyl groups are relatively short.[4] In relation to the study on block copolymers, a homopolymer of **3** (**8**) having one perfluoroethyl group at its initiating end was prepared by the polymerization of **3a** with 3-methyl-2-(pentafluoroethyl)-2-oxazolinium trifluoromethanesulfonate as initiator (Scheme II).

Surface Activity of the Block Copolymer. Every system shows the clear critical micelle concentration (cmc) as indicated by the inflection points in the plots of surface tension value of an aqueous solution of the block copolymer **6** and **7** versus the logarithm of concentration. The cmc values are listed in Table II. The cmc values of **6b** samples are of a similar magnitude to those of **6a**. On the other hand, the values of **6c** samples, which have poly(**3b**) as hydrophilic chains instead of poly(**3a**), are lower than those of both **6a** and **6b**. At present, the reason for this is not well understood, but this may be ascribed to the large difference in their molecular conformations in aqueous solution. The cmc values are in the range 0.0024–0.027 wt %, which are quite good in comparison with those of fluoroalkyl-containing surfactants previously reported,[8] i.e., derivatives of poly(oxyethylene),[6,7] tertiary ammonium salt,[9] sulfobetaine,[9] and amino acid and carboxylic acid salts.[10,11]

Surface tension values at cmc and those at the concentration of 0.1 wt % are summarized in Table II. In the series **6a** with the short hydrophilic chains, i.e., **6a**-1 and **6a**-4, the surface tension value tends to decrease with increasing concentration beyond the cmc. Presumably, the length of the hydrophilic chain is not enough to form stable micelles.

It can be said that **6b** and **6c** copolymers represent better surface activities than **6a**. This is presumably due to the higher hydrophobicity of the perfluoro-*n*-propyl group compared to that of the perfluoroethyl group.

It is also to be noted here that the surfactants with a shorter hydrophilic chain show excellent surface activity. Especially, **6c**-1 exhibits a very low surface tension value, which is one of the best values among fluoroalkyl-containing surfactants.

It is evident that the surface tension of the solution of **7** is slightly higher than that of the corresponding **6**. However, all of the series **7** show clear cmc's, which are generally at lower levels in comparison with the values of **6a**. It is assumed that **7** is readily ordered at the surface of the solution even at low concentration, since the in-

Scheme II

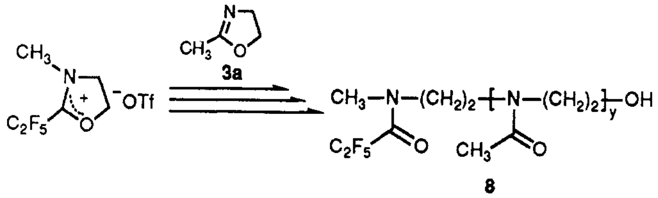


Table II
Surface Activities

sample	structure[a] x[a]	y[a]	fluorine, content, wt %	cmc,[b] wt %	surface tension, dyn/cm at cmc[c]	at 0.1%[c]
6a-1	2.7	5.5	25.3	0.018	19.1	15.0
6a-2	2.7	7.3	22.0	0.005	27.9	25.9
6a-3	2.7	11.1	17.3	0.005	28.8	25.1
6a-4	5.4[d]	6.0[e]	32.8	0.012	29.4	23.1
6a-5	5.4[d]	10.9[e]	25.9	0.010	25.2	23.8
6a-6	5.4[d]	20.7[e]	18.2	0.027	30.0	32.0
6b-1	2.8	3.4	37.6	0.022	25.9	19.6
6b-2	2.8	4.4	34.0	0.009	19.8	20.7
6b-3	2.8	7.6	22.0	0.008	25.0	25.7
6c-1	2.9	3.2	37.0	0.0024	15.0	12.8
6c-2	2.9	5.4	30.6	0.0025	18.9	16.7
6c-3	2.9	10.4	22.0	0.0029	28.0	28.1
7-1	2.7	3.6	29.3	0.007	28.4	26.1
7-2	2.7	5.2	24.0	0.006	27.2	28.5
7-3	2.7	9.2	16.2	0.006	30.5	29.0
8-1	1	2.0	23.8			23.1
8-2	1	3.4	18.6			16.3
8-3	1	4.3	16.4			18.7

[a] See Scheme I, x and y were calculated from molecular weight data by VPO unless otherwise indicated. [b] Critical micelle concentrations given by the plots of surface tension versus concentration. [c] The surface tension was measured at 20 °C with a Wilhelmy-type tensiometer. [d] Determined by ^1H NMR spectra. [e] Calculated from the N:F ratio of elemental analysis.

troduction of a trimethylene spacer between perfluoroalkyl groups, instead of ethylene group in the case of **6a**, makes the rotation of the perfluoroalkyl groups easier. The surface tension of **7** tends to decrease with decreasing the length of 2-methyl-2-oxazoline polymer unit as shown in the other cases.

Between the two series of samples **6a**-1–3 and **6a**-4–6, there is no significant difference in surface tension values. Thus, the length of hydrophobic chain in this region does not influence cmc nor γ_{cmc}. However, in the case of the homopolymer having one perfluoroethyl group, **8**, the plots of γ value versus concentration shows no clear cmc. Thus, it can be concluded that the polymer having only one short perfluoroethyl group at the polymer end is not a "surface active agent". And since the short perfluoroalkyl group is not arranged at water surface, it is concluded that the introduction of a set of several short perfluoroalkyl groups in the pendant groups of the same chain is required to exhibit surface activity. In addition, the high performance may be due to low surface energy of compactly aligned terminal CF_3 groups.[12] Thus, the short sequence of small perfluoroalkyl groups functions as an excellent hydrophobic component of non-ionic surfactant. The comb-like structure of the block copolymer assists the orientation of perfluoroalkyl group on the surface.

Experimental Section

Materials. 2-(Pentafluoroethyl)-2-oxazoline (**1a**), 2-(heptafluoro-*n*-propyl)-2-oxazoline (**1b**), 2-(pentafluoroethyl)-5,6-dihydro-4*H*-1,3-oxazine (**2**), and 3-methyl-2-(pentafluoroethyl)-2-oxazolinium trifluoromethanesulfonate were prepared as described before.[4] Commercially available 2-methyl-2-oxazoline (**3a**), 2-ethyl-2-oxazoline (**3b**), and methyl trifluoromethanesulfonate were purified by repeated distillation under nitrogen. Nitromethane was purified by repeated distillation under nitrogen and stored over molecular sieves 3 Å.

Measurements. ^1H NMR spectra were recorded on a 60-MHz Hitachi R-600 or a 400-MHz JEOL-JNM-GX400 NMR spectrometer. ^{19}F NMR spectra were obtained on a Hitachi R-900 NMR spectrometer at 84.7 MHz, and chemical shifts are given relative to external CF_3CO_2H. Molecular weight determination was carried out by a vapor pressure osmometer, Hitachi Model 117 or Hitachi Model 114, in $CHCl_3$ or acetonitrile, respectively, at 40 °C. GPC analysis was performed by using a TSK-GEL G2500H column in DMF containing 0.4% triethylamine at 50 °C. The surface tension of the aqueous solution of surfactants was measured at 20 °C by a Wilhelmy-type tensiometer, Kyowa CBVP Surface Tensiometer A 1 (Japan), with varying concentration.

One-Pot Two-Stage Polymerization. A typical procedure was as follows. In a glass tube was dissolved 0.192 g of methyl trifluoromethanesulfonate (1.17 mmol) in 3.372 g of nitromethane, and 0.714 g of **2** (3.51 mmol) was added at 0 °C under nitrogen. The tube was sealed and kept at 70 °C for 12 h. After the first-stage polymerization was completed, the tube was opened and the reaction mixture was divided into four portions. One of them was poured into an excess amount of a 50/50 mixture of diethyl ether and hexane. The polymeric materials were collected and dried in vacuo to give pale yellow powdery materials. **5** (entry 5-0): 400-MHz ^1H NMR (CD_3NO_2) δ 2.28–2.42 (br, CCH_2C), 3.18–3.26 (br, CH_3N), 3.44–3.64 (br, CH_2N), 3.64–3.71 (br, CH_2OH); ^{19}F NMR (CD_3NO_2) δ −37.92, −35.97 (br, CF_2, 2 F), −5.69 (br, CF_3, 3 F).

The second portion of the reaction mixture (1.45 g) was transferred to a new glass tube under nitrogen, and then 1.19 mmol of **3a** and 0.5 mL of nitromethane were added. The tube was sealed and kept at 70 °C for 12 h (second stage). After working up according to the similar procedure, the block copolymer was successfully isolated. **7-1** (entry 5-1): 60-MHz ^1H NMR ($CDCl_3$) δ 1.6–2.5 (br, CCH_2C and $CH_3C{=}O$), 2.9–3.9 (br, CH_3N and CH_2N).

Preparation of 8. A typical run was as follows. Into an ice-cooled ampule containing 0.346 g of 3-methyl-2-(pentafluoroethyl)-2-oxazolinium trifluoromethanesulfonate (0.979 mmol) dissolved in 1 mL of nitromethane was added 0.255 g of **3a** (3.00 mmol) under nitrogen. The ampule was sealed and kept at 70 °C for 20 h. The oligomer, **8-1**, was obtained by reprecipitation from a 50/50 mixture of diethyl ether and hexane in 55% yield. **8-1**: 60-MHz ^1H NMR ($CDCl_3$) δ 2.1 (br, $CH_3C{=}O$), 3.2 (br, CH_3N), 3.5 (br, CH_2N).

Acknowledgment. We thank Professor Yoshiyuki Sano of Shiga Prefectural Junior College for his permission and kind advice in using the Wilhelmy-type tensiometer.

Registry No. (**1a**)(**3a**) (block copolymer), 120666-03-7; (**1b**)(**3a**) (block copolymer), 120666-04-8; (**1b**)(**3b**) (block copolymer), 120666-05-9; (**2a**)(**3a**) (block copolymer), 120666-07-1.

References and Notes

(1) Kobayashi, S.; Igarashi, T.; Moriuchi, Y.; Saegusa, T. *Macromolecules* **1986**, *19*, 535.

(2) (a) Litt, M. H.; Chen, T. T.; Hsieh, B. R. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 3407. (b) Litt, M. H.; Hsieh, B. R.; Krieger, I. M.; Chen, T. T.; Lu, H. L. *J. Colloid Interface Sci.* **1987**, *115*, 312.

(3) Schick, M. J., Ed. *Nonionic Surfactants*; Marcel Dekker Inc.: New York, 1967.

(4) Miyamoto, M.; Aoi, K.; Saegusa, T. *Macromolecules* **1988**, *21*, 1880.

(5) Ramharack, R.; Nguyen, T. H. *J. Polym. Sci., Part C: Polym. Lett.* **1987**, *25*, 93.

(6) Selve, C.; Castro, B. *Tetrahedron* **1983**, *39*, 1313.

(7) Tatematsu, R.; Ozaki, S.; Nagase, S.; Inukai, K., *Yukagaku* **1976**, *25*, 287 (Japanese); *Chem. Abstr.* **1976**, *85*, 93732h.

(8) Ishikawa, N. *Yukagaku* **1977**, *26*, 613 (Japanese); *Chem. Abstr.* **1978**, *88*, 39230s.

(9) Kimura, C.; Murai, K.; Kashiwaya, K.; Kanno, T.; Nishiyama, T. *Yukagaku* **1982**, *31*, 464 (Japanese); *Chem. Abstr.* **1982**, *97*, 129468r.

(10) Kimura, C.; Kashiwaya, K.; Kobayashi, M.; Murai, K.; Nishiyama, T. *Yukagaku*, **1984**, *33*, 838 (English); *Chem. Abstr.* **1985**, *102*, 80771q.

(11) Kunieda, H.; Shinoda, K. *J. Phys. Chem.* **1976**, *80*, 2468.

(12) (a) Hare, E. F.; Shafrin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1954**, *58*, 236. (b) Shafrin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1962**, *66*, 740.