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Block Copolymers from Cyclic Imino Ethers: A New Class of Nonionic Polymer Surfactant

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ABSTRACT: Various types of block copolymers from cyclic imino ether monomers have been designed and prepared by utilizing the living nature of the cationic ring-opening polymerization of the monomers. Block copolymers prepared are AB and BA type diblock (**3**) and ABA and BAB type triblock copolymers (**5** and **9**). All copolymers consist of a hydrophilic chain (A block) and a lipophilic chain (B block). The chains are of an amide type structure. The monomers used are seven 2-substituted 2-oxazolines (OZO) and three (unsubstituted and two 2-substituted) 5,6-dihydro-4*H*-1,3-oxazines (OZI). 2-Methyl-2-oxazoline (MeOZO) was used most often for construction of an effective hydrophilic block of an *N*-acetylethylenimine unit. 2-*n*-Butyl- (BuOZO), 2-*n*-octyl- (OcOZO), 2-*n*-dodecyl- (DoOZO), and 2-phenyl-2-oxazolines (PhOZO) produce a lipophilic block. These block copolymers exhibit excellent surface activities and, hence, are a group of nonionic polymer surfactants. The surface activities reflected by the surface tension (γ) in water are very high: a γ value as low as 27.5 dyn/cm for an AB type diblock copolymer from MeOZO/BuOZO and 23.7 dyn/cm for a BAB type triblock copolymer from MeOZO/OcOZO. One characteristic of the present polyamide type surfactants is that they do not show a clouding point.

Cationic ring-opening polymerization of cyclic imino ethers is a versatile, convenient method to prepare linear poly(*N*-acylalkylenimines).[1] During the course of our studies on the polymerization of cyclic imino ethers, we have found that poly(*N*-acetylethylenimine) is highly hygroscopic and possesses a good hydrophilic property. These findings prompted us to prepare block copolymers from cyclic imino ethers, which contain both hydrophilic and lipophilic chains in the same molecule and, hence, are expected to exhibit surfactant properties. The present paper reports the synthesis and surfactant properties of AB and BA type diblock and ABA and BAB type triblock copolymers derived from cyclic imino ethers. Throughout this paper A and B blocks represent hydrophilic and lipophilic blocks, respectively.

Results and Discussion

I. Diblock Copolymers. The synthesis of AB type block copolymers **3** utilizes a "one-pot two-stage copolymerization" technique on the basis of the mechanistic living nature of the cationic polymerization; i.e., one of cyclic imino ethers **1**, such as 2-methyl-2-oxazoline (MeOZO), is first polymerized (the first stage) to give A block, and, then, the other monomer **2** (e.g., 2-*n*-butyl-2-oxazoline (BuOZO), is polymerized by the living ends of the first polymerization system (the second stage) to give B block.

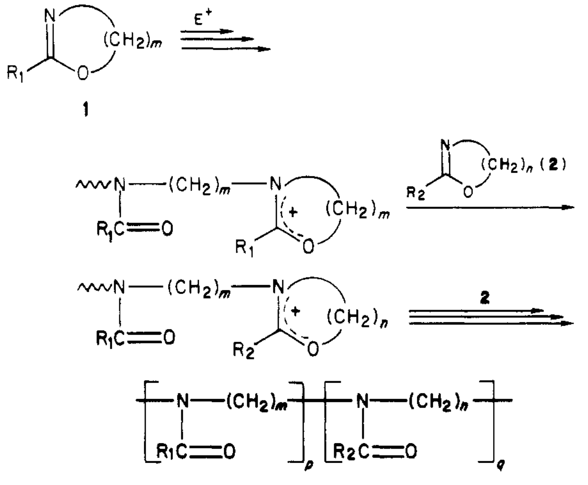
0024-9297/86/2219-0535$01.50/0

Table I
Block Copolymerization and Copolymers of 2-Methyl-2-oxazoline (MeOZO) and 2-Phenyl-2-oxazoline (PhOZO)[a]

	block copolymerization						block copolymer (3a)		
	1st stage			2nd stage					
entry no.	$[MeOZO]_0$/$[MeOTs]_0$	temp, °C	time, h	$[PhOZO]_0$/$[MeOTs]_0$	temp, °C	time, h	mol wt by VPO	unit ratio[b] (*p*:*q*)	γ,[c] dyn/cm
1-0	5.2	80	15	0			720	6.3:0	70.8
1-1	5.2	80	15	5.2	100	18	1630	6.3:6.2	52.1
1-2	5.2	80	15	10.1	100	18	2420	6.3:11.6	52.5
1-3	5.2	80	15	14.8	100	18	2890	6.3:14.8	54.6
2-0	11.3	80	15	0			1250	12.5:0	
2-1	11.3	80	15	7.5	100	18	2410	12.5:7.9	48.3
3-0	15.4	80	15	0			1720	18.0:0	70.0
3-1	15.4	80	15	4.9	100	16	2350	18.0:4.3	48.9
3-2	15.4	80	15	10.4	100	16	3040	18.0:9.0	51.2
4-0	20.8	80	30	0			2060	22.0:0	67.8
4-1	20.8	80	30	14.3	100	33	4170	22.0:14.4	51.2
4-2	20.8	80	30	21.3	100	33	5030	22.0:20.2	53.4
4-3	20.8	80	30	32.7	100	33	6610	22.0:31.0	57.3

[a] MeOTs initiator in CH_3CN. Copolymer yields were almost quantitative (>97%) in all cases. [b] The ratio of the first monomer to the second monomer was determined on the basis that the respective polymer contains one molecule of MeOTs. [c] The surface tension was measured with a Du Noüy tensiometer with the polymer concentration of 1.0 wt %, which is higher than the critical micelle concentration, at 29 °C (γ of water at 29 °C = 71.3 dyn/cm).

Among various copolymers **3**, **3h** and **3i** are BA type structures.



3a, R_1 = Me; R_2 = Ph; *m* = *n* = 2
b, R_1 = Et; R_2 = Ph; *m* = *n* = 2
c, R_1 = Me; R_2 = Et; *m* = *n* = 2
d, R_1 = Me; R_2 = *n*-Pr; *m* = *n* = 2
e, R_1 = Me; R_2 = *n*-Bu; *m* = *n* = 2
f, R_1 = Me; R_2 = *n*-Oc; *m* = *n* = 2
g, R_1 = Me; R_2 = *n*-Do; *m* = *n* = 2
h, R_1 = *n*-Bu; R_2 = Me; *m* = *n* = 2
i, R_1 = Et; R_2 = Me, *m* = *n* = 2
j, R_1 = Me; R_2 = Ph; *m* = 2; *n* = 3
k, R_1 = H; R_2 = Ph; *m* = 3; *n* = 2
l, R_1 = Me; R_2 = Ph; *m* = 3; *n* = 2
m, R_1 = H; R_2 = Ph; *m* = *n* = 3
n, R_1 = Me; R_2 = Ph; *m* = *n* = 3

Block Copolymers of 2-Methyl-2-oxazoline and 2-Phenyl-2-oxazoline. The block copolymerization of 2-methyl-2-oxazoline (MeOZO) as the first monomer with 2-phenyl-2-oxazoline (PhOZO) as the second monomer was carried out by changing the molar ratio of the monomers. For example, the polymerization of MeOZO (17.8 mmol) with 3.4 mmol of methyl tosylate (MeOTs) initiator in 5.0 mL of acetonitrile at 80 °C for 15 h constitutes the first-stage polymerization. It was confirmed by ^1H NMR spectroscopy that the MeOZO had been consumed completely. Then the reaction mixture was divided into four parts. The polymerization of one part was stopped (entry no. 1). To the remaining three parts were added 2.9, 4.4, and 5.1 mmol of PhOZO, respectively, and the mixtures were kept at 100 °C for 18 h, which constitutes the second-stage polymerization. Then the mixtures were subjected to workup procedures to produce block copolymers quantitatively (entries no. 1-1, 1-2, and 1-3, respectively).

The ^1H NMR spectrum ($CDCl_3$) of copolymer no. 1-1 showed singlets at δ 2.1 ($CH_3C{=}O$), 2.3 (CH_3Ar), 3.0 (CH_3N), 2.9–3.9 (br, CH_2N) 7.0–7.6 (br, $C_6H_5C{=}O$) overlapping with an A_2B_2 quartet at δ 7.1 and 7.7 ($MeC_6H_4SO_3$). From the integral ratio of the signals due to CH_3Ar, $CH_3C{=}O$, and $C_6H_5C{=}O$, the copolymer composition of MeOZO:PhOZO = 5.6:6.1 was obtained based on the assumption that MeOTs is contained in each copolymer molecule. This composition is very close to that obtained from the molecular weight data (6.3:6.2) (Table I).

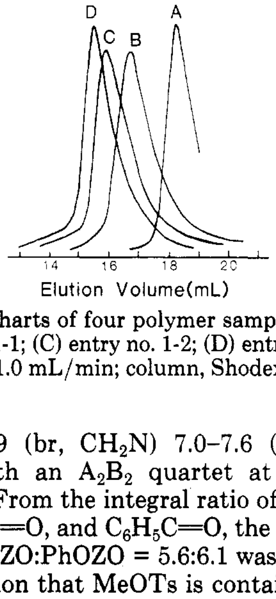
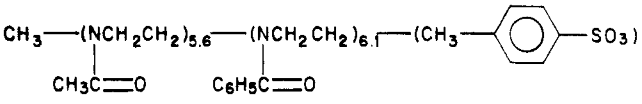


Figure 1. GPC charts of four polymer samples: (A) entry no. 1-0; (B) entry no. 1-1; (C) entry no. 1-2; (D) entry no. 1-3. Eluent, $CHCl_3$; flow rate, 1.0 mL/min; column, Shodex A803 with an RI detector.

The copolymer formation was clearly proved by gel permeation chromatography (GPC). GPC charts of these copolymers (**3a**) are shown in Figure 1. All copolymers exhibited a single peak, from which the molecular weight distribution evaluated by M_W/M_N was calculated as follows: 1.07 for entry no. 1-0, 1.29 for entry no. 1-1, 1.31 for entry no. 1-2, and 1.22 for entry no. 1-3. These data indicate that the molecular weight distribution is very narrow, and hence the copolymerization is living without involving side reactions such as chain-transfer or termination. Furthermore, the peak position comes earlier with the copolymer having a longer PhOZO chain. This was confirmed also by the vapor pressure osmometry (VPO) of the copolymers.



$$CH_3\!-\!(\underset{\displaystyle CH_3C{=}O}{N}CH_2CH_2)_{5.6}\!-\!(\underset{\displaystyle C_6H_5C{=}O}{N}CH_2CH_2)_{6.1}\!-\!(CH_3\!-\!C_6H_4\!-\!SO_3)$$

3a

Table I shows results with varying ratios of monomers and MeOTs initiator. It is seen that the length of co-

Table II
Block Copolymerizations and Copolymers of Various 2-Oxazolines[a]

			block copolymerization						block copolymer 3			
			1st stage			2nd stage						
entry no.	1st monom	2nd monom	$[1st monom]_0$/$[MeOTs]_0$	temp, °C	time, h	$[2nd monom]_0$/$[MeOTs]_0$	temp, °C	time, h	structure	mol wt by VPO	unit ratio[b] (p:q)	γ,[b] dyn/cm
5-0	EtOZO	PhOZO	10.4	80	15	0			**3b**	1330	11.5:0	52.6
5-1			10.4	80	15	5.0	100	18	**3b**	2040	11.5:4.8	51.0
5-2			10.4	80	15	9.9	100	18	**3b**	2930	11.5:10.8	49.5
6	MeOZO	EtOZO	4.7	80	16	5.0	100	24	**3c**	1170	5.4:5.3	52.9
7	MeOZO	PrOZO	4.7	80	16	4.8	100	24	**3d**	1310	5.4:5.8	48.4
8-1	MeOZO	BuOZO	5.1	80	16	4.8	100	33	**3e**	1320	5.5:5.3	30.9
8-2			5.0	80	16	13.8	100	33	**3e**	2310	5.9:12.8	32.8
9-1	MeOZO	OcOZO	5.1	80	16	5.8	100	33	**3f**	1550	5.5:4.9	32.1
9-2			9.9	80	16	5.4	100	33	**3f**	1940	11.3:4.3	32.8
10-1	MeOZO	DoOZO	5.2	80	15	4.4	100	46	**3g**	1730	6.3:4.2	37.4
10-2			15.4	80	15	5.1	100	46	**3g**	2700	18.0:4.1	46.6
11	BuOZO	MeOZO	4.9	80	10	6.7	80	15	**3h**	1560	6.3:6.8	33.6
12	EtOZO	MeOZO	6.0	80	10	5.7	80	15	**3i**	1490	7.2:6.9	57.3

[a] MeOTs initiator in CH_3CN. Copolymer yields were almost quantitative. EtOZO, 2-ethyl-2-oxazoline; PrOZO, 2-*n*-propyl-2-oxazoline; BuOZO, 2-*n*-butyl-2-oxazoline; OcOZO, 2-*n*-octyl-2-oxazoline; DoOZO, 2-*n*-dodecyl-2-oxazoline. [b] Determined in a similar manner as those in Table I.

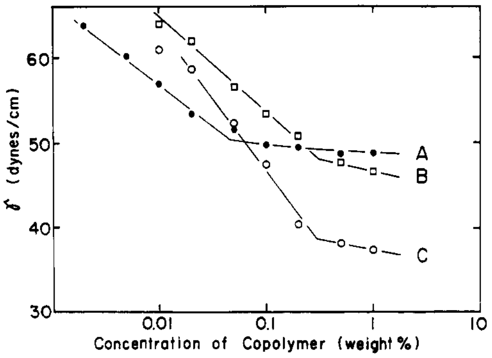


Figure 2. Copolymer concentration–γ relationships: (A) sample no. 2-1; (B) sample no. 10-2; (C) sample no. 10-1.

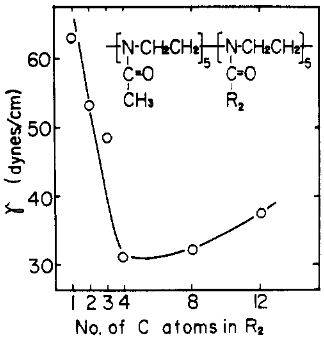


Figure 3. Relationship between the γ value and the chain length of alkyl group R_2.

polymer chain of both the first and second stages is governed mainly by the monomer-to-MeOTs ratio. Therefore, the copolymer composition and molecular weight control can be easily achieved by controlling the ratios of the first monomer to MeOTs and of the second monomer to MeOTs.

All copolymer samples **3a** are soluble in water, methanol, chloroform, etc. **3a** consists of a hydrophilic poly(*N*-acetylethylenimine) chain and a lipophilic poly(*N*-benzoylethylenimine) chain, which is, hence, expected to exhibit surfactant properties. As an indication of the surfactant nature, the surface tension (γ) was measured in water, whose values are given in Table I. The γ values were obtained with aqueous polymer solutions of 1.0 wt %, which was higher than the critical micelle concentration (cmc) as shown in Figure 2. A copolymer sample (no. 2-1) exhibited the cmc value below 0.1 wt %. Homopolymers of MeOZO (no. 1-0, 3-0, and 4-0) showed virtually no surfactant properties. On the other hand, all samples of **3a** exhibited moderately good surfactant properties and reached γ = 48.3 dyn/cm (no. 2-1). Molecular weight does not affect γ values much.

Acute toxicity has been examined on samples no. 2-1 and 3-2. The sample amount of 2.0 g/kg was given orally to five mice, and all mice were alive after 7 days; i.e., LD_{50} > 2 g/kg (mouse). With similar experiments for sodium dodecylbenzenesulfonate (DBS), a typical ionic surfactant, the survival was 20%; i.e., $LD_{50} \lesssim 2$ g/kg (mouse). This value is in good agreement with a reported value of $LD_{50} \sim 2.0$ g/kg (mouse) for DBS.[2] In addition, samples no. 2-1 and 3-2 did not show toxic symptoms for digestive organs of mice. These results can be taken to indicate that acute toxicity of copolymers **3a** is very low.

Block Copolymers from Various 2-Oxazolines. Similarly, one-pot two-stage copolymerizations have been carried out for the following combinations: 2-ethyl-2-oxazoline (EtOZO)/PhOZO, MeOZO/EtOZO, MeOZO/2-*n*-propyl-2-oxazoline (PrOZO), MeOZO/2-*n*-butyl-2-oxazoline (BuOZO), MeOZO/2-*n*-octyl-2-oxazoline (OcOZO), MeOZO/2-*n*-dodecyl-2-oxazoline (DoOZO), BuOZO/MeOZO, and EtOZO/MeOZO. These copolymers are of AB type except for the last two, which are of BA type. These copolymerization results are given in Table II, which includes molecular weight data as well as unit ratio values (p:q) of the first monomer to the second monomer in the copolymer. All copolymers **3** showed a single peak by GPC analysis and are soluble in water.

Surface activities reflected by the surface tension (γ) are dependent upon the nature of R_1 and R_2 as well as the values of p and q. The γ values of **3b** from EtOZO/PhOZO are slightly larger than those of **3a**, indicating a less hydrophilic nature of the polymer chain of EtOZO than that of MeOZO.

With R_1 as a methyl group and p:q as ~5:~5, the effect of the R_2 group on the surface tension was examined (entry no. 6-10). As seen in Figure 3, alkyl groups of C_4–C_{12} are appropriate for the effective surface activity as R_2 which constitutes a lipophilic chain. These alkyl groups are better than phenyl group. Copolymers from MeOZO/EtOZO and MeOZO/PrOZO combinations are probably not lipophilic enough.

The cmc value of copolymers **3f** (no. 10-1 and 10-2) was below 0.3 wt % (Figure 2).

The order of the monomer feed can be reversed in the present one-pot two-stage copolymerizations (entry no. 11

Table III
Effects of the Composition (p/q Ratio) on the Surface Tension of Copolymers of MeOZO/BuOZO and MeOZO/OcOZO[a]

entry no.	R_1	R_2	mol wt by VPO	p	q	p:q	γ,[b] dyn/cm
8-2	CH_3	n-C_4H_9	2310	5.9	12.8	0.46	32.8
8-3	CH_3	n-C_4H_9	2410	8.2	12.0	0.68	31.4
8-4	CH_3	n-C_4H_9	2310	11.0	9.4	1.17	31.1
8-5	CH_3	n-C_4H_9	2370	14.0	7.8	1.79	28.9
8-6	CH_3	n-C_4H_9	2430	18.8	5.0	3.76	27.5
9-3	CH_3	n-C_8H_{17}	2740	5.5	11.4	0.48	42.4
9-1	CH_3	n-C_8H_{17}	1550	5.5	4.9	1.12	32.1
9-2	CH_3	n-C_8H_{17}	1940	11.3	4.3	2.63	32.8

[a] All copolymers were prepared analogously to entry no. 8-1 and 9-1. [b] Determined in a similar manner as those in Table I.

Table IV
Block Copolymerizations and Copolymers Involving 1,3-Oxazines[a]

			block copolymerization						block copolymers 3			
			1st stage			2nd stage						
entry no.	1st monom	2nd monom	$[\text{1st monom}]_0/[\text{MeOTs}]_0$	temp, °C	time, h	$[\text{1st monom}]_0/[\text{MeOTs}]_0$	temp, °C	time, h	structure	mol wt by VPO	unit ratio[b] (p:q)	γ,[b] dyn/cm
13-1	MeOZO	PhOZI	10.5	80	15	6.5	100	44	**3j**	2310	11.5:7.3	46.5
13-2			10.5	80	15	11.7	100	44	**3j**	3240	11.5:12.8	
14	OZI	PhOZO	9.9	100	25	5.5	100	15	**3k**	2650	14.4:8.5	52.0
15-0	MeOZI	PhOZO	9.9	100	40	0			**3l**	1230	10.5:0	64.9
15-1			9.9	100	40	5.6	100	40	**3l**	2060	10.5:5.6	48.4
15-2			9.9	100	40	11.0	100	40	**3l**	2680	10.5:9.9	51.0
16	OZI	PhOZI	10.1	100	25	5.1	100	31	**3m**	2310	13.4:6.1	52.5
17-1	MeOZI	PhOZI	9.9	100	40	5.9	100	40	**3n**	1940	10.5:4.4	46.6
17-2			9.9	100	40	9.3	100	40	**3n**	2640	10.5:8.8	49.9

[a] MeOTs initiator in CH_3CN. Copolymer yields were almost quantitative or very high. OZI, 1,3-oxazine; MeOZI, 2-methyl-1,3-oxazine; PhOZI, 2-phenyl-1,3-oxazine. [b] Determined in a similar manner as those in Table I.

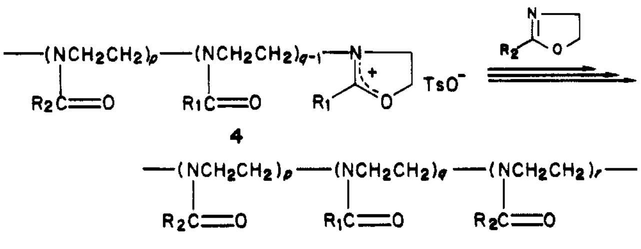
and 12). In both cases the designed copolymers (**3h** and **3i**) were produced. They showed one peak by GPC analysis. The copolymer from BuOZO/MeOZO showed as a good surfactant nature as that from MeOZO/BuOZO.

Since combinations of MeOZO/BuOZO and MeOZO/OcOZO are found to be very suitable, these have been examined in more detail. Table III shows effects of the composition of AB type block copolymers (p:q ratio) on the surface tension. In entry no. 8-2–8-6, the molecular weight of the copolymers was controlled in a narrow range. The γ value decreases monotonously by increasing the p:q ratio within the range examined (p:q = 0.46–3.76). The best surfactant properties are observed for sample no. 8-6 as γ = 27.5 dyn/cm. In entry no. 9-3, 9-1, and 9-2, n-octyl group was employed. Copolymers of the p:q ratio of 1.12 and 2.63 show good surfactant properties.

As to block copolymers **3**, a similar type of block copolymers consisting of, e.g., poly(N-propionylethylenimine) and poly(N-dodecanoylethylenimine) chains have been prepared, and their surface tension was measured in chloroform, ethylene glycol, or methanol/water (80/20).[3] These copolymers, therefore, are not completely soluble in water. Thus, the block copolymers **3** in the present study are to be taken as a nonionic polymer surfactant soluble in water. It should be also mentioned that poly(N-acylethylenimine) was used as a hydrophilic chain for construction of polymer surfactants, in which a lipophilic initiator was employed to induce the polymerization of 2-oxazolines like MeOZO or EtOZO.[4]

Block Copolymers Involving 1,3-Oxazines. A class of six-membered cyclic imino ethers, 5,6-dihydro-4H-1,3-oxazines (1,3-oxazines, OZI) have been employed for constructing a hydrophilic or lipophilic chain. In one-pot two-stage copolymerizations, a cyclic imino ether producing a hydrophilic chain (A block) is used as the first monomer and the one forming a lipophilic chain (B block) as the second monomer. Thus, OZI and 2-methyl-1,3-oxazine (MeOZI) are the former and 2-phenyl-1,3-oxazine (PhOZI) is the latter (Table IV). All copolymers showed a single peak by GPC analysis and are soluble in water except for sample no. 13-2, which is less soluble in water. The homopolymer of MeOZI poly(N-acetyltrimethylenimine) (entry no. 15-0) is essentially not a surfactant. But all block copolymers show moderately good surfactant properties as reflected by γ values.

II. Triblock Copolymers. From Monofunctional Initiator (Sequential Method). It has been shown above that the one-pot two-stage copolymerization can be performed either by forming a hydrophilic chain at the first stage and a lipophilic chain at the second stage or by forming the polymer chains in the reverse way. It is also clear that OZO monomers are more suitable for a hydrophilic or lipophilic chain than OZI monomers and that OZO monomers are more readily accessible than OZI monomers. On the basis of these observations, the one-pot two-stage copolymerization has been extended to the preparation of BAB type triblock copolymers from 2-oxazolines via one-pot three-stage copolymerization. With MeOTs initiator the propagating ends are given by **4** after the first and second stages are over. Then, the first monomer is polymerized again by **4** to give rise to a BAB type triblock copolymer **5**. This copolymerization can be carried out successively in one pot.



4

5a, R_2 = n-Bu; R_1 = Me
b, R_2 = n-Oc; R_1 = Me
c, R_2 = Me; R_1 = n-Bu

Table V
BAB Type Triblock Copolymers from 2-Oxazolines by the Sequential Method

				block copolymerization[a]			block copolymers 5			
entry no.	1st monom	2nd monom	3rd monom	1st stage $\frac{[\text{1st monom}]_0}{[\text{MeOTs}]_0}$	2nd stage $\frac{[\text{2nd monom}]_0}{[\text{MeOTs}]_0}$	3rd stage $\frac{[\text{3rd monom}]_0}{[\text{MeOTs}]_0}$	structure	mol wt by VPO	unit ratio[b] *p*:*q*:*r*	γ,[b] dyn/cm
18-0	BuOZO	MeOZO	BuOZO	5.2	0	0		950	6.0:0:0	insol
18-1				5.2	10.5	0	**(3h)**	1880	6.0:10.9:0	32.6
18-2				5.2	10.5	5.2	**5a**	2540	6.0:10.9:5.2	31.3
19-0	OcOZO	MeOZO	OcOZO	5.3	0	0		1230	5.7:0:0	insol
19-1				5.3	5.3	0		1720	5.7:5.8:0	33.0
19-2				5.3	5.3	4.7	**5b**	2660	5.7:5.8:5.1	23.7
19-3				5.3	10.8	0		1990	5.7:8.9:0	35.2
19-4				5.3	10.8	5.3	**5b**	2990	5.7:8.9:5.5	30.3

[a] Polymerization was carried out with MeOTs initiator in CH_3CN at 80 °C for 30 h (the first stage), for 38 h (the second stage), and for 40 h (the third stage). [b] Determined in a similar manner as those in Table I except for the measurement temperature of γ, which was 20 °C (γ of water at 20 °C = 72.8 dyn/cm).

Table VI
ABA Type Triblock Copolymers from 2-Methyl-2-oxazoline (MeOZO) and 2-*n*-Butyl-2-oxazoline (BuOZO) by the Sequential Method

	block copolymerization[a]			block copolymers			
entry no.	1st stage $\frac{[\text{MeOZO}]_0}{[\text{MeOTs}]_0}$	2nd stage $\frac{[\text{BuOZO}]_0}{[\text{MeOTs}]_0}$	3rd stage $\frac{[\text{MeOZO}]_0}{[\text{MeOTs}]_0}$	structure	mol wt by VPO	unit ratio[b] *p*:*q*:*r*	γ,[b] dyn/cm
20-0	5.4	0	0		740	6.5:0:0	70.9
20-1	5.4	9.8	0	**3e**	1880	6.5:9.0:0	32.5
20-2	5.4	9.8	5.7	**5c**	2360	6.5:9.0:5.6	35.8

[a] Polymerization was carried out with MeOTs initiator in CH_3CN at 80 °C for 31 h (the first stage), for 35 h (the 2nd stage), and for 33 h (the 3rd stage). [b] Determined in a similar manner as those in Table V.

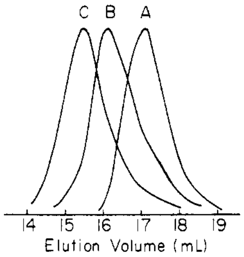


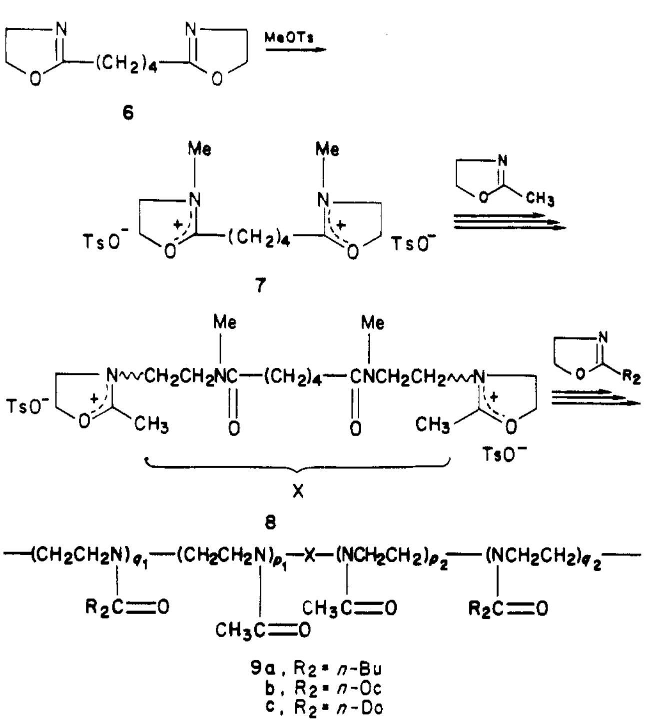
Figure 4. GPC charts of three polymer samples: (A) entry no. 18-0; (B) entry no. 18-1; (C) entry no. 18-2. Eluent, $CHCl_3$; flow rate, 1.0 mL/min; column, Shodex A803 with an RI detector.

Table V shows the copolymerization results in which are used MeOZO for a hydrophilic chain (A block) at the second stage and BuOZO or OcOZO for a lipophilic chain (B block) at the first and third stages. The yield of copolymers was quantitative or very high. The monomer-to-initiator ratio at each stage is very close to the average chain length (*p*, *q*, and *r*) of the copolymer produced. These findings indicate that the copolymerization is of fast initiation and of living system. GPC analysis gave additional support for these findings. In the combination of BuOZO/MeOZO/BuOZO, the homopolymer of BuOZO (no. 18-0), BA type diblock copolymer (no. 18-1), and BAB type triblock copolymer (no. 18-2) all show a respective single peak (Figure 4). Furthermore, the molecular weight distribution reflected by M_W/M_N values of these polymers is very narrow: M_W/M_N = 1.12 for sample 18-0, 1.19 for sample 18-1, and 1.21 for sample 18-2.

Surface properties of these block copolymers are excellent, e.g., $\gamma < 35$ dyn/cm. Surface activities are better in BAB type triblock copolymers than in BA type diblock copolymers. It is striking that the value of sample no. 19-2 reaches 23.7 dyn/cm, showing a very strong surface activity. In the BAB type copolymers, both lipophilic chains are linked by a central hydrophilic chain and are likely to be in a more ordered structure in water than in the BA type copolymer.

On the other hand, an ABA type block copolymer was also prepared via the sequential method. MeOZO and BuOZO were used to build up A and B blocks, respectively, to give copolymer **5c** (Table VI). GPC charts of AB type copolymer (no. 20-1) and **5c** (no. 20-2) showed a single peak, indicating that the copolymerization at the first and the second stages proceeded in a manner of living system. The surface activity of **5c**, however, was less than that of AB type copolymer (no. 20-1) from γ values. This is probably due to a less ordered structure of the lipophilic chain B of **5c** in water in comparison with that of the AB type copolymer. But this view is not conclusive, i.e., the surface activity of an ABA type copolymer is not necessarily superior to that of an AB type copolymer or to that of a BAB type copolymer. Further studies are required to clarify this respect.

From Bifunctional Initiator. Another way to prepare BAB type triblock copolymers is to start from a bifunctional initiator and to make it propagate at both ends via two-stage copolymerizations in one pot. For this purpose, 2,2′-tetramethylenebis(2-oxazoline) (**6**) was prepared and subjected to reaction with two equimolar amount of MeOTs to produce bis(tosylate) **7**. The salt **7** was isolated. First, MeOZO was polymerized by the salt to form a hydrophilic chain (A block). The second stage is the polymerization of a second monomer by the living species at both ends of **8**. The second monomers used are BuOZO, OcOZO, and DoOZO, which give a lipophilic chain (B block). Thus, BAB type triblock copolymers **9** have been prepared via two-stage polymerization. All copolymers of **9** were obtained quantitatively and showed a broad, yet single, peak by GPC analysis. The surface tension of **9** was examined (Table VII). Polymers obtained by the first stage (no. 21-0 and 22-0) do not show a low γ value. Copolymers **9** exhibit a lower value. With $p_1 + p_2 = 11.8$ and



21.8, the nature of R_2 was examined under the $q_1 + q_2$ value of 7.5–9.5. Then, copolymer **9** from BuOZO (no. 21-1) showed the lowest γ value of 27.6 dyn/cm. Copolymers from DoOZO do not have as good a surfactant nature as others.

This method does not necessarily require the isolation of bis(tosylate) **7**. The preparation of **7** in situ makes the copolymerization feasible in one pot.

The above two methods for preparing BAB type triblock copolymers offer general methods to prepare multiblock copolymers from cyclic imino ethers.

Finally, all the above copolymers consist of hydrophilic chain(s) (A blocks) and lipophilic chain(s) (B blocks) and exhibit surface-active properties in a variety of monomer combinations and in a wide range of block length. The surface tension (γ) was determined as a measure of the surface activities of copolymers. It is known that γ values are highly dependent on the nature of the hydrophilic and lipophilic parts and their balance (HLB). It is possible that further experiments to adjust these factors will permit development of copolymers showing a stronger surface-active nature. It should be added that all the copolymers are soluble in water except no. 13-2 and that they seem not to exhibit a clouding point, i.e., a water solution of entry no. 1-1, 1-2, 1-3, 2-1, 3-1, and 3-2 did not become turbid even when warmed up to nearly boiling. The present block copolymers are very low in acute toxicity and are to be compared with polyether type nonionic polymer surfactants ("Pluronics"),[5] in which poly(ethylene oxide) and poly(propylene oxide) chains are used as hydrophilic and lipophilic blocks, respectively. Polyether type surfactants show a clouding point. No clouding point for the present copolymers is probably due to a strong hydrogen bonding between water and the copolymers because of the highly polarized nature of the amide structure. Very recently, we have prepared poly[(2-phenyl-2-oxazoline)-*g*-(ethylene oxide)] by using a macromer technique.[6] It is mentioned here that this graft copolymer showed very efficient surfactant properties because of the structure of the lipophilic main chain and the hydrophilic graft chain.

Experimental Section

Materials. Solvents, CH_3CN, and diethyl ether were purified in a usual manner. A commercial reagent of MeOZO (Aldrich Chemical Co.) and EtOZO given by Dow Chemical Co. were purified by distillation. Monomers PrOZO, OcOZO, and DoOZO were prepared according to the literature.[7] Three 1,3-oxazine monomers, OZI, MeOZI, and PhOZI, were obtained as reported previously.[8] 2,2′-Tetramethylenebis(2-oxazoline) (**6**) was prepared from 1,4-dicyanobutane and 2-aminoethanol as reported,[7] bp 110–115 °C (0.6 mmHg). A commercial reagent of MeOTs was purified by distillation. All distillations were carried out under nitrogen.

Two-Stage Copolymerization for Diblock Copolymer. A typical run was as follows. In a glass tube was dissolved 17.8 mmol of MeOZO in 5.0 mL of acetonitrile, and 3.4 mmol of MeOTs was added at 0 °C under nitrogen. The tube was sealed and kept at 80 °C for 15 h. After this first-stage polymerization was completed, the tube was opened and the reaction mixture was divided into four parts. Three parts (1.01 g, 0.78 g, and 0.63 g) were transferred to three new glass tubes under nitrogen. The remaining reaction mixture (3.62 g) was poured into 50 mL of diethyl ether to precipitate a polymeric material. After reprecipitation with aceonitrile as a solvent and diethyl ether as a nonsolvent, the polymeric material was collected and dried in vacuo to give 1.20 g of pale yellowish powdery material (95% yield, entry no. 1-0). To the foregoing three glass tubes containing the reaction mixtures were added 2.9, 4.4, and 5.1 mmol of PhOZO, respectively, and then 0.1, 0.5, and 0.88 mL of acetonitrile, respectively. These glass tubes were sealed and kept at 100 °C for 18 h. After this second-stage polymerization was completed, each reaction mixture was poured into 50 mL of diethyl ether to precipitate polymeric materials. After reprecipitation (acetonitrile–diethyl ether), the polymeric materials were collected and dried in vacuo to give 0.76 g (97% yield, entry no. 1-1), 0.89 g (98% yield, entry no. 1-2), and 0.87 g (90% yield, entry no. 1-3) of pale yellowish powdery materials. Molecular weight data for these four polymers by VPO are given in Table I. ^{1}H NMR (entry no. 1-1 in $CDCl_3$) δ 2.1 (s, $CH_3C{=}O$), 2.3 (s, CH_3Ar), 3.0 (s, CH_3N), 2.9–3.9 (br, CH_2N), 7.0–7.6 (br, $C_6H_5C{=}O$), 7.1 and 7.7 (q, $MeC_6H_4SO_3$). Anal. Calcd for $C_{33.2}H_{54.1}N_{6.3}O_{9.3}S_{1.0}$ (entry no. 1-0): C, 55.20; H, 7.55; N, 12.22. Found: C, 55.51; H, 7.61; N, 11.90. Anal. Calcd for $C_{89.0}H_{109.9}N_{12.5}O_{15.5}S_{1.0}$ (entry no. 1-1): C, 65.39; H, 6.78; N, 10.71. Found: C, 65.48; H, 6.63; N, 10.64. Anal. Calcd for $C_{137.6}H_{158.5}N_{17.9}O_{20.9}S_{1.0}$ (entry no. 1-2): C, 68.02; H, 6.58; N, 10.32. Found: C, 68.26; H, 6.43; N, 10.26. Anal. Calcd for $C_{166.4}H_{187.3}N_{21.1}O_{24.1}S_{1.0}$ (entry no. 1-3): C, 68.90; H, 6.51; N, 10.19. Found: C, 68.84; H, 6.36; N, 9.99.

Three-Stage Copolymerization for Triblock Copolymer. A typical run was as follows. In a glass tube was dissolved 5.9 mmol of BuOZO in 2.5 mL of acetonitrile, and 1.1 mmol of MeOTs was added at 0 °C under nitrogen. The tube was sealed and kept at 80 °C for 30 h. After this first-stage polymerization was completed, the reaction mixture was divided into two parts. One part (1.39 g) was transferred to another glass tube. To this tube was added 5.6 mmol of MeOZO and 1.2 mL of acetonitrile. After being sealed, the tube was kept at 80 °C for 38 h (second-stage polymerization). The remaining reaction mixture was transferred to a flask, and acetonitrile was evaporated in vacuo. The remaining polymeric material was dried in vacuo to give 0.45 g of a white powdery material (95% yield, entry no. 18-0). After the second-stage polymerization was completed, the reaction mixture was divided into two parts again. One part (1.44 g) was transferred to a new glass tube. To this tube was added 1.4 mmol of BuOZO. After being sealed, the tube was kept at 80 °C for 40 h (third-stage polymerization). The remaining reaction mixture was poured into 50 mL of diethyl ether to precipitate a polymeric material. After reprecipitation (acetonitrile–diethyl ether), the polymeric material was collected and dried in vacuo to give 0.43 g of a white powdery material (93% yield, entry no. 18-1). After the third-stage polymerization was completed, the reaction mixture was poured into 50 mL of diethyl ether to precipitate a polymeric material. After reprecipitation (acetonitrile–diethyl ether), the polymeric material was collected and dried in vacuo to give 0.64 g of a white powdery material (97% yield, entry no. 18-2). ^{1}H NMR (entry no. 18-2 in $CDCl_3$) δ 0.7–1.2 (br, CH_3C), 1.0–1.9 (br, CH_2C), 2.1 (s, $CH_3C{=}O$), 2.0–2.6 (br, $CH_2C{=}O$), 2.4 (s, CH_3Ar), 3.0 (s, CH_3N), 2.9–3.9 (br, CH_2N), 7.1, 7.7 (q, $C\text{-}C_6H_4SO_2$). Molecular weight data for these three polymers are given in Table V. Anal. Calcd for $C_{50.0}H_{88.0}N_{6.0}O_{9.0}S_{1.0}$ (entry no. 18-0): C, 63.26; H, 9.34; N, 8.85;

Table VII
Triblock Copolymers from 2-Oxazolines by Using Bifunctional Initiator

	block copolymerization[a]			block copolymers **9**			
	1st stage	2nd stage					
entry no.	$[MeOZO]_0/{}^1/_2[7]_0$	R_2	$[R_2OZO]_0/{}^1/_2[7]_0$	structure	mol wt by VPO	unit ratio[b] $(p_1 + p_2):(q_1 + q_2)$	γ,[b] dyn/cm
21-0	10.8		0		1570	11.8:0	63.5
21-1	10.8	n-C_4H_9	9.7	**9a**	2780	11.8:9.5	27.6
21-2	10.8	n-C_8H_{17}	9.0	**9b**	2990	11.8:7.8	34.4
21-3	10.8	n-$C_{12}H_{25}$	8.8	**9c**	3440	11.8:7.8	46.2
22-0	21.2		0		2420	21.8:0	57.2
22-1	21.2	n-C_4H_9	10.4	**9a**	3510	21.8:8.6	31.2
22-2	21.2	n-C_8H_{17}	9.9	**9b**	3820	21.8:7.7	39.0
22-3	21.2	n-$C_{12}H_{25}$	9.8	**9c**	4190	21.8:7.4	49.7

[a] Polymerization was performed with bis(tosylate) **7** in CH_3CN at 80 °C for 25 h (the first stage) and at 100 °C for 25 h (the second stage). [b] Determined in a similar manner as those in Table V.

S, 3.38. Found: C, 63.07; H, 9.74; N, 8.71; S, 3.36. Anal. Calcd for $C_{93.6}H_{164.3}N_{16.9}O_{19.9}S_{1.0}$ (entry no. 18-1): C, 59.89; H, 8.82; N, 12.61; S, 1.71. Found: C, 60.19; H, 9.05; N, 12.55; S, 1.75. Anal. Calcd for $C_{130.0}H_{231.9}N_{22.1}O_{25.1}S_{1.0}$ (entry no. 18-2): C, 61.51; H, 9.21; N, 12.20; S, 1.26. Found: C, 61.52; H, 9.39; N, 12.06; S, 1.24.

Preparation of Bifunctional Initiator: *N,N'*-Dimethyl-2,2'-tetramethylenebis(oxazolinium tosylate) (7). All operations were carried out under nitrogen. To a mixture of 3.0 mL of diethyl ether and 16.2 mmol of MeOTs in a glass tube was added 2.7 mmol of 2,2'-tetramethylenebis-2-(oxazoline) (**6**) at 0 °C. The tube was sealed and kept at 80 °C for 2 h. The reaction mixture was poured into 30 mL of diethyl ether to precipitate *N,N'*-dimethyl-2,2'-tetramethylenebis(oxazolinium tosylate) (**7**), which was separated by filtration and washed with diethyl ether three times. The isolated white solid was purified by reprecipitation (solvent was acetonitrile and nonsolvent was diethyl ether) twice to give 0.94 g of **7** (61% yield). ^{1}H NMR (CD_3CN) δ 1.7 (br, CCH_2CH_2C, 4 H), 2.4 (s, CH_3Ar, 6 H), 2.7 (br, $(CNO)CH_2$, 4 H), 3.2 (s, NCH_3, 6 H), 4.1 (t, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2O}$, 4 H), 4.8 (t, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{O}$, 4 H), 7.2 and 7.7 (2 d, CC_6H_4S, 8 H).

Two-Stage Copolymerization for Triblock Copolymer. A typical run was as follows. Into a glass tube containing 1.2 mmol of *N,N'*-dimethyl-2,2'-tetramethylenebis(oxazolinium tosylate) (**7**) dissolved in 5.7 mL of acetonitrile was added 12.6 mmol of MeOZO under nitrogen. The tube was sealed and kept at 80 °C for 25 h. After this first-stage polymerization was completed, the reaction mixture was divided into four parts. Three parts (1.48 g, 1.47 g, and 1.33 g) were transferred into three new glass tubes under nitrogen. The remaining reaction mixture was poured into 50 mL of diethyl ether to precipitate a polymeric material. After reprecipitation (acetonitrile as solvent and diethyl ether as nonsolvent), the polymeric material was collected and dried in vacuo to give 0.49 g of a pale yellowish powdery material (96% yield, entry no. 21-0). To the foregoing three new glass tubes containing the reaction mixtures were added under nitrogen 2.7 mmol of BuOZO, 2.5 mmol of OcOZO, and 2.2 mmol of DoOZO, respectively. These glass tubes were sealed and kept at 100 °C for 25 h. After the second-stage polymerization was completed, each reaction mixture was transferred to a flask and the acetonitrile was evaporated in vacuo. The remaining polymeric materials were dried in vacuo to give 0.73 g of a pale yellowish powdery material (98% yield, entry no. 21-1), 0.81 g of a pale yellowish powdery material (95% yield, entry no. 21-2), and 0.84 g of a pale brownish material (94% yield, entry no. 21-3). ^{1}H NMR of sample entry no. 21-0 ($CDCl_3$) δ 1.7 (br, $\mathrm{NC({=}O)CH_2C}\mathit{H}_2$), 2.0 (s, $C({=}O)CH_3$), 2.3 (s, $C({=}O)CH_2$), 2.4 (s, $ArCH_3$), 2.8 (br, $NC({=}O)CH_2$), 3.0 (NCH_3), 2.9–3.9 (br, NCH_2), 4.1, 4.8 (m, NCH_2CH_2O), 7.2, 7.7 (q, $O_3SC_6H_4C$). ^{1}H NMR of sample entry no. 21-1 ($CDCl_3$) δ 0.7–1.2 (br CCH_3), 1.0–1.9 (br, CCH_2C), 2.0 (s, $CH_3C{=}O$) 2.0–2.6 (br, $CH_2C{=}O$), 2.4 (s, $ArCH_3$), 3.0 (s, NCH_3), 2.9–3.9 (br, CH_2N), 7.2, 7.7 (2 d, $O_3SC_6H_4C$). ^{1}H NMR signal positions of samples entry no. 21-2 and 21-3 were much the same as those of sample entry no. 21-1.

Measurements. ^{1}H NMR spectra were recorded on a 60-MHz Hitachi R-20B NMR spectrometer at 35 °C with a Me_4Si standard. The molecular weight of the polymers was measured by a Corona 117 vapor pressure osmometer in chloroform at 40 °C. For the molecular weight distributions of polymers, gel permeation chromatography (GPC) analysis was performed by using a Jasco TRIROTOR with an RI detector under the following conditions: column, Shodex A 803; solvent, chloroform; flow rate, 1 mL/min. The surface tension of aqueous polymer solutions (1.0 wt %) was measured by a Shimadzu Du Noüy tensiometer.

Registry No. MeOTs, 80-48-8; (MeOZO)·(PhOZO) (copolymer), 40082-04-0; (EtOZO)·(PhOZO) (copolymer), 30373-14-9; (MeOZO)·(EtOZO) (copolymer), 25931-20-8; (MeOZO)·(PrOZO) (copolymer), 28086-96-6; (MeOZO)·(BuOZO) (copolymer), 99811-02-6; (MeOZO)·(OcOZO) (copolymer), 99811-03-7; (MeOZO)·(DoOZO) (copolymer), 95038-97-4; (MeOZO)·(PhOZI) (copolymer), 95038-98-5; (OZI)·(PhOZO) (copolymer), 99811-04-8; (MeOZI)·(PhOZO) (copolymer), 99811-05-9; (OZI)·(PhOZI) (copolymer), 99811-06-0; (MeOZI)·(PhOZI) (copolymer), 99811-07-1.

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