*n*-Butyllithium was purchased from Aldrich. Its concentration was determined by double titration.[7]

HMPA was distilled from calcium hydride and stored over activated 4-Å molecular sieves.

**1,1-Dimethyl-1-silacyclopent-3-ene** (I) was prepared by the reaction of dimethyldichlorosilane, 1,3-butadiene, and magnesium in THF.[8,9]

**1,1-Diphenyl-1-silacyclopent-3-ene** (II) was prepared by the reaction of diphenyldichlorosilane, 1,3-butadiene, and magnesium in THF.[8,10]

**Copolymerization of I and II** was carried out under an atmosphere of argon with standard syringe–septa techniques. A 50-mL flame-dried Schlenk flask equipped with a Teflon-covered magnetic stirring bar was rinsed with 20 mL of 0.5 M *n*-butyllithium in THF. In this flask was then placed I (1.1 g, 10 mmol), II (see Table I for ratio of I to II), six drops of HMPA, and 20 mL of THF. The reaction mixture was then cooled to −50 °C. *n*-Butyllithium in hexane (10 mol % to I and II) was added with stirring. A brown color appeared immediately. The reaction mixture was kept at −50 °C for 2 h and then warmed to −10 °C. A 10-mL solution of saturated aqueous ammonium chloride was added. The aqueous layer was separated and extracted with 40 mL of ether 3 times. The combined organic layer was washed with water until the aqueous layer was neutral. The organic layer was dried over 4-Å molecular sieves. Ether was removed by evaporation under reduced pressure. The crude copolymer was dissolved in THF and was then precipitated by addition of the copolymer solution to an excess of methanol. The supernatant was found by GLPC to quantitatively contain unreacted starting monomers I and II. The copolymers were dried under vacuum for 2 days. Yields are given in Table I. All copolymers have similar IR $\nu$: 3060, 3040, 3000, 2960, 2940, 1630, 1420, 1370, 1240, 1145, 1100, 1015 $\text{cm}^{-1}$.

**Acknowledgment.** This work was supported in part by the Air Force Office of Scientific Research 89-0007 and the Office of Naval Research. We thank Dr. C. Juengst for help in obtained DSC measurements.

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**Registry No.** (I)(II) (copolymer), 125050-22-8.

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# Block Copolymerization of Tetrahydrofuran with Cyclic Imino Ether: Synthesis of a New Nonionic Polymer Surfactant

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ABSTRACT: Block copolymers from tetrahydrofuran (THF) and cyclic imino ethers were synthesized in one pot by utilizing the living nature of the cationic ring-opening polymerization of both monomers. Block copolymers prepared are AB-type diblock and BAB-type triblock copolymers. The polymers had a hydrophobic poly(oxytetramethylene) segment (A block) from THF and a hydrophilic poly(*N*-acylalkylenimine) segment (B block) from the cyclic imino ether. Cyclic imino ether monomers used for construction of the hydrophilic segment are 2-methyl- and 2-ethyl-2-oxazolines and 2-methyl-5,6-dihydro-4*H*-1,3-oxazine. These block copolymers exhibit excellent surface activities and, hence, are a group of nonionic polymer surfactants. The surface activities reflected by the surface tension ($\gamma$) in water are very high. The lowest $\gamma$ value reached 28.2 dyn/cm for a BAB-type triblock copolymer from THF/2-methyl-2-oxazoline.

## Introduction

Cationic ring-opening polymerization of cyclic imino ethers is conveniently employed to prepare linear poly(*N*-acylalkylenimines).[1] Various block copolymers containing poly(*N*-acylalkylenimines) segments were synthesized by the polymerization of cyclic imino ethers initiated with a polymer having iodide or a *p*-toluenesulfonic acid ester group.[2] In using this initiator, the rate of initiation was slower than that of propagation and it was difficult, therefore, to control the length of poly(*N*-acylalkylenimine) segment.

Recently we have found that a poly(*N*-acylalkylenimine) becomes hydrophilic or hydrophobic by changing of the nature of the acyl group. We have paid attention to this property and synthesized a new nonionic polymer surfactant by utilizing the living nature of the cationic polymerization of cyclic imino ethers.[3] One-pot, two-stage and one-pot, three-stage copolymerizations afforded AB- and ABA- (or BAB-) type block copolymers, respec-

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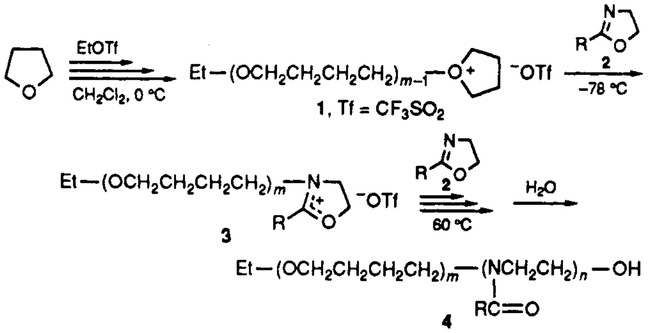
0024-9297/90/2223-1586$02.50/0

tively, in which A or B denotes a hydrophilic or hydrophobic polymer chain. These copolymers possess both hydrophilic and hydrophobic chains in the same molecules and, hence, showed very good surfactant properties evaluated by the surface tension ($\gamma$) of copolymers in water.

The present paper reports the one-pot synthesis and surfactant properties of block copolymers consisting of a hydrophobic poly(oxytetramethylene) segment and a hydrophilic poly(*N*-acylalkylenimine) segment. To construct a hydrophilic polymer segment, monomers used are 2-methyl- and 2-ethyl-2-oxazolines (MeOZO and EtOZO, respectively) and 2-methyl-5,6-dihydro-4*H*-1,3-oxazine (MeOZI).

## Results and Discussion

**Synthesis of Diblock Copolymers.** It is well-known that an anhydride or ester of superacids such as $CF_3SO_3H$ gives a living polymerization of THF.[4] The polymerization of THF was performed with ethyl trifluoromethanesulfonate (EtOTf) as an initiator in $CH_2Cl_2$ at 0 °C for 1 h to produce the living propagating species **1** of polyTHF. Then a cyclic imino ether **2** was added to the polymerization mixture at −78 °C and allowed to react for 1 h to produce polyTHF having an oxazolinium group at the terminal **3**. Then the polymerization of **2** was carried out using **3** as initiator to give the block copolymer between polyTHF and poly(*N*-acylalkylenimine) (**4**).



Under the present reaction conditions, the degree of THF polymerization was small at the first stage of copolymerization. With the addition of a cyclic imino ether monomer **2** at the second stage, the polymerization of **2** was induced immediately by the THF living species **1**. Then the polymerization of **2** took place exclusively even if unreacted THF was present because of the big difference in reactivity of propagating species between both monomers, **2** and THF.

The structure of **4** was confirmed by IR and $^1$H NMR spectroscopy.[5] From the $^1$H NMR spectrum of **4**, the unit ratio (*m*:*n*) was calculated by the integral ratio of signals a and b (Figure 1). The composition was determined from the unit ratio and the molecular weight obtained by vapor pressure osmometry (VPO). Block copolymerization results are given in Table I. The *n* value of poly(*N*-acylethylenimine) from **2** is very close to that of the charged [**2**]/[EtOTf], which implies that the living end of polyTHF **1** reacts with **2** quantitatively to form polymer **3** having the oxazolinium group at the end, and the polymerization of **2** by **3** is a fast initiation system as reported previously.[6] According to gel permeation chromatography (GPC), all polymer samples **4** showed only one narrow peak ($M_w/M_n \sim 1.10$–$1.31$), supporting strongly that **4** is the block copolymer of THF and **2**.

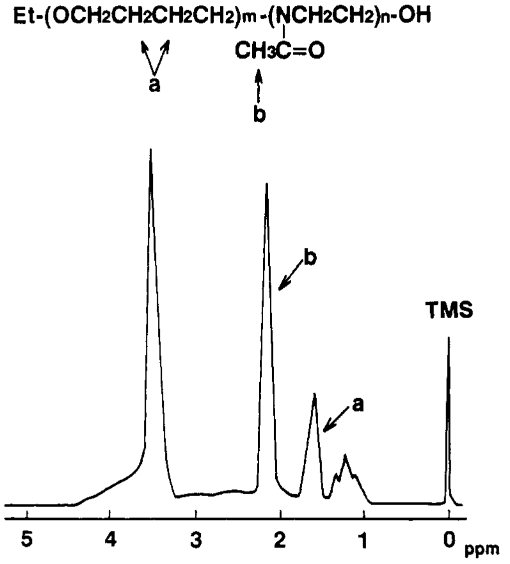


**Figure 1.** 60-MHz $^1$H NMR spectrum of diblock copolymer **4** (entry 2).

An attempt was made to calculate the expected $M_n$ value on the basis of the experimental results of, e.g., entry 1 in Table I. Assuming that the number of the product copolymer molecules **4** is equal to that of the initiator EtOTf, the expected $M_n$ is yield (g)/mol of EtOTf = 455, which is not so much different from the observed value of 600. By this calculation, the expected $M_n$ values were somewhat smaller than the observed ones in all cases. This tendency is more characteristic of the copolymer having a longer THF chain. These results are explained as follows. Copolymer **4** was isolated by reprecipitation from chloroform (solvent) and *n*-hexane (nonsolvent). During this procedure, a portion of **4** containing a longer THF chain was soluble in *n*-hexane and therefore was lost, which brought about the decreased yield of **4**.

The surfactant properties of polymer **4** were evaluated by measuring the surface tension ($\gamma$) in water. The $\gamma$ 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. All samples showed good surfactant properties. Among the polymers prepared, polymer sample 2 exhibited the lowest $\gamma$ value of 30.1 dyn/cm. As a whole, the longer chain length of poly(*N*-acylethylenimine) (*n*) in **4** did not exhibit better surfactant properties. The change of the monomer for construction of a hydrophilic segment is small in the present reaction involving a short polyTHF chain, indicating that the hydrophilic nature of the polymer segment obtained by polymerization of MeOZO, EtOZO, and MeOZI is sufficient. Appropriate hydrophilic–lipophilic balance (HLB) may be achieved when the chain length of poly(oxytetramethylene) (*m*) is ca. 2 and *n* is 4–6.

**Synthesis of Triblock Copolymers.** The method to prepare BAB-type triblock copolymers is to start from a bifunctional initiator and to allow the propagation at both ends via a two-stage copolymerization in one pot. For this purpose, trifluoromethanesulfonic anhydride ($Tf_2O$) was used.

Initiation of THF by a superacid anhydride like $(ClSO_2)_2O$ is fast.[7] In fact, under the present reaction conditions $Tf_2O$ had been consumed completely, checked by $^{19}$F NMR, before a cyclic imino ether monomer was added to induce the second-stage polymerization. Accordingly, the chain length of poly(*N*-acylethylenimine) ($l$ + $n$) in **5** is very close to the feed [**2**]/[$Tf_2O$] ratio and the

**Table I**
**Diblock Copolymerization and Copolymers of THF and 2-Oxazolines**

| | block copolymerization[a] | | | | | block copolymer 4 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | EtOTf, mmol | THF, mmol | $CH_2Cl_2$, mL | R | [ROZO]/[EtOTf] | yield, g | $M_n$[b] | $m$[c] | $n$[c] | $M_w/M_n$[d] | $\gamma$[e] |
| 1 | 0.567 | 78.5 | 13.5 | Me | 5.3 | 0.258 | 600 | 1.0 | 5.6 | 1.18 | 37.1 |
| 2 | 0.949 | 104 | 11.7 | Me | 5.2 | 0.362 | 670 | 1.7 | 5.9 | 1.11 | 30.1 |
| 3 | 0.463 | 106 | 10.8 | Me | 5.7 | 0.253 | 635 | 2.5 | 4.8 | 1.12 | 33.1 |
| 4 | 0.663 | 82.6 | 13.1 | Me | 9.8 | 0.496 | 997 | 1.1 | 10.2 | 1.20 | 40.8 |
| 5 | 1.06 | 194 | 23.3 | Me | 14.2 | 0.587 | 1420 | 3.6 | 13.1 | 1.26 | 42.1 |
| 6 | 1.08 | 104 | 10.9 | Et | 4.8 | 0.307 | 645 | 0.7 | 5.5 | 1.13 | 40.0 |
| 7 | 0.797 | 94.5 | 20.2 | Et | 4.7 | 0.431 | 594 | 1.7 | 4.3 | 1.22 | 33.7 |
| 8 | 1.13 | 101 | 11.2 | Et | 9.5 | 0.823 | 1040 | 1.0 | 9.3 | 1.22 | 40.7 |
| 9 | 1.75 | 194 | 38.8 | Et | 9.2 | 1.77 | 1160 | 1.8 | 9.9 | 1.31 | 41.9 |
| 10 | 0.780 | 101 | 11.5 | MeOZI[f] | 4.8 | 0.237 | 778 | | | 1.10 | 40.8 |

[a] Polymerization of THF was carried out at 0 °C for 1 h and then the polymerization of 2-oxazolines was carried out at 60 °C for 24 h. [b] From VPO. [c] From VPO and $^1H$ NMR. [d] Obtained by GPC. [e] The surface tension ($\gamma$) was measured with a Du Noüy tensiometer with the polymer concentration = 1.0 wt %, which is higher than the critical micelle concentration at ambient temperature and recalculated to the value at 25 °C. [f] 2-Methyl-5,6-dihydro-4*H*-1,3-oxazine was used as monomer.

**Table II**
**Triblock Copolymerization and Copolymers of THF and 2-Oxazolines**

| | block copolymerization[a] | | | | | block copolymer 5 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | $Tf_2O$, mmol | THF, mmol | $CH_2Cl_2$, mL | R | [ROZO]/[$Tf_2O$] | yield, g | $M_n$[b] | $m$[c] | $l + n$[c] | $M_w/M_n$[d] | $\gamma$[e] |
| 11 | 0.751 | 56.3 | 20.0 | Me | 5.8 | 0.544 | 763 | 3.5 | 5.6 | 1.28 | 42.1 |
| 12 | 0.755 | 73.1 | 20.0 | Me | 8.1 | 0.642 | 1000 | 3.3 | 7.9 | 1.20 | 28.2 |
| 13 | 0.572 | 81.7 | 13.8 | Me | 10.2 | 0.409 | 1880 | 9.2 | 11.6 | 1.25 | 40.7 |
| 14 | 0.794 | 58.9 | 15.2 | Me | 19.0 | 1.38 | 2040 | 5.7 | 18.9 | 1.30 | 45.8 |
| 15 | 0.872 | 70.8 | 19.7 | Et | 7.7 | 0.872 | 1090 | 2.4 | 8.4 | 1.29 | 28.6 |
| 16 | 0.526 | 87.7 | 13.9 | MeOZI[f] | 10.2 | 0.586 | 1280 | | | 1.31 | 35.1 |

[a] Polymerization of THF was carried out at 0 °C for 1 h and then the polymerization of 2-oxazoline was carried out at 60 °C for 24 h. [b] From VPO. [c] From VPO and $^1H$ NMR. [d] Obtained by GPC. [e] Determined in a similar way as those in Table I. [f] 2-Methyl-5,6-dihydro-4*H*-1,3-oxazine was used as monomer.

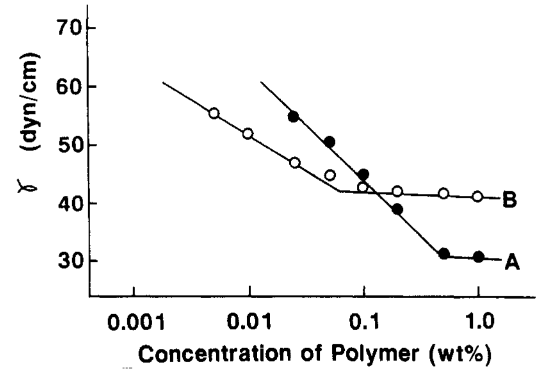


Figure 2. Polymer concentration-$\gamma$ relationships: (A) polymer sample of entry 2; (B) polymer sample of entry 4.

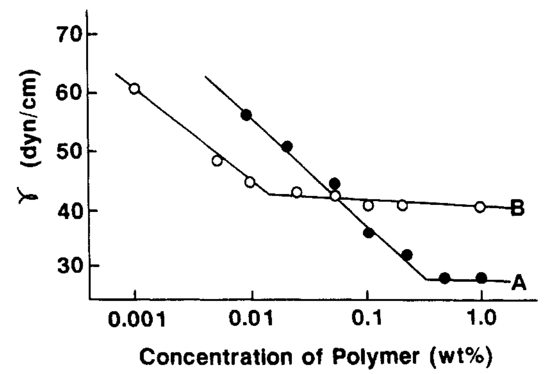
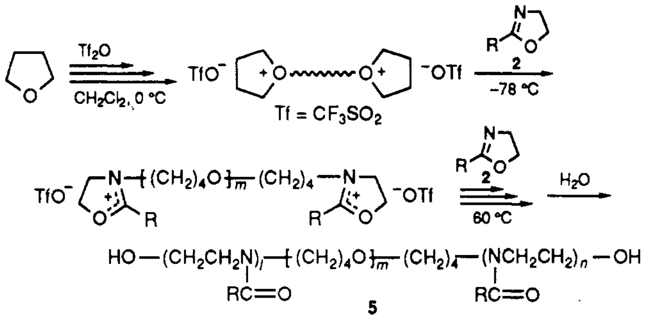


Figure 3. Polymer concentration-$\gamma$ relationships: (A) polymer sample of entry 12; (B) polymer sample of entry 13.



molecular weight distribution evaluated by $M_w/M_n$ was very narrow in all cases (Table II). The expected $M_n$ value of, e.g., entry 11 in Table II was also calculated as yield (g)/mol of $Tf_2O$ = 724, which is very close to the observed $M_n$ of 763. In other cases, expected $M_n$ values were close to observed ones, except for entry 13. Copolymer **5** of entry 13 contains a longer THF chain relative to the *N*-acetylethylenimine chain; a large portion of **5** was lost by the reprecipitation procedure using *n*-hexane as a nonsolvent. These observations support that all the initiator $Tf_2O$ produced copolymers **5**.

Surface properties of these block copolymers are excellent, e.g., $\gamma < 30$ dyn/cm in two cases. Surface activities are better in BAB-type block copolymers than those in AB-type diblock copolymers. Figure 3 indicates the $\gamma$-value dependency on the polymer concentration. The cmc values were smaller than 1.0 wt % in all cases. The longer chain of the hydrophobic segment is not necessarily good for better surface properties of **5**. Appropriate HLB may be achieved with $m$ and $n$ values of around 3 and 8, respectively.

## Experimental Section

**Materials.** Solvent $CH_2Cl_2$ was purified by distillation twice over calcium hydride. Commerical reagent THF was purified by distillation three times over lithium aluminium hydride before use. Commercial reagents EtOTf, MeOZO, and EtOZO were purified by distillation. Commercial reagent $Tf_2O$ was purified by distillation over $P_2O_5$. MeOZI was prepared according to the literature.[8] All operations were carried out under nitrogen.

**Synthesis of Diblock Copolymers.** A typical run was as follows (entry 4). To the solution of 5.96 g (82.6 mmol) of THF in 13.1 mL of $CH_2Cl_2$, 0.108 g (0.606 mmol) of EtOTf was added at 0 °C under nitrogen. The polymerization of THF was carried out for 1 h at 0 °C and the reaction mixture cooled to −78 °C. To the mixture was added 0.503 g (5.91 mmol) of MeOZO and this was allowed to react at −78 °C for 1 h. Then, the mixture was transferred to a glass tube under nitrogen and the tube was sealed and kept at 60 °C for 24 h. The tube was opened and the mixture was poured into a saturated $Na_2CO_3$ aqueous solution (50 mL) and stirred for 1 h. The mixture that resulted was extracted with chloroform (30 mL × 3) and the organic layer was separated and dried over $MgSO_4$. After evaporation of the solvent and reprecipitation (chloroform–*n*-hexane), the polymeric material was collected and dried in vacuo to give 0.449 g of **4**: $^1$H NMR ($CDCl_3$) $\delta$ 1.0–1.4 (m, $CH_3C$), 1.5–2.0 (br, $CCH_2C$), 2.1 (s, $CH_3C{=}O$), 2.5–2.7 (m, $CCH_2N$), 3.1–4.1 (br, $CCH_2N$ and $CCH_2O$); IR (neat) 3400 ($\nu_{O-H}$), 1630 cm$^{-1}$ ($\nu_{C=O}$). Anal. Calcd for $C_{47.2}H_{86.2}N_{10.2}O_{12.3}(H_2O)_{2.0}$, (hygroscopic): C, 55.07; H, 8.83; N, 13.88. Found: C, 54.70; H, 9.34; N, 13.76.

**Synthesis of Triblock Copolymers.** A typical run was as follows (entry 12). To a THF solution (5.27 g, 73.1 mmol) in 14.0 mL of $CH_2Cl_2$, 0.213 g (0.755 mmol) of $Tf_2O$ was added at 0 °C under nitrogen. The polymerization of THF was carried out at 0 °C for 1 h, followed by cooling to −78 °C. To the polymerization mixture, 0.552 g (6.12 mmol) of MeOZO was added and this stood at −78 °C for 1 h. Then the mixture was transferred into a glass tube, which was sealed and kept at 60 °C for 24 h. After the tube was opened, the mixture was poured into a saturated $Na_2CO_3$ aqueous solution (50 mL) and extracted with chloroform (30 mL × 3). Then the organic layer was dried over $MgSO_4$, followed by evaporation. The residue was dissolved in 3 mL of chloroform. The mixture was poured into 80 mL of *n*-hexane to precipitate the polymeric materials, followed by filtration to give 0.644 g of **5**: $^1$H NMR ($CDCl_3$) $\delta$ 1.5–2.0 (br, $CCH_2C$), 2.0 (s, $CH_3C{=}O$), 2.5–2.7 (m, $CCH_2N$), 3.1–4.1 (br, $CCH_2N$ and $CCH_2O$); IR (neat) 3400 ($\nu_{O-H}$), 1630 cm$^{-1}$ ($\nu_{C=O}$).

**Measurements.** $^1$H NMR spectra were recorded on a 60-MHz Hitachi R-600 NMR spectrometer. IR spectra were recorded on a Hitachi 260-50 spectrometer. The molecular weights of polymers were measured by a Corona 117 vapor pressure osmometer in chloroform at 40 °C. Gel permeation chromatographic (GPC) analysis was performed by using a JASCO TRIROTOR with RI and UV detectors under the following conditions: Shodex K-802 or AC-803 column with chloroform eluent at a flow rate of 1.0 mL/min. The surface tension ($\gamma$) of aqueous polymer solutions was measured by a Shimadzu Du Noüy tensiometer at ambient temperature and the $\gamma$ values obtained were recalculated to the values at 25 °C.

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**Registry No.** EtOTf, 425-75-2; (MeOZO)(THF) (block copolymer), 125050-23-9; (EtOZO)(THF) (block copolymer), 125050-25-1; (MeOZT)(THF) (block copolymer), 125050-26-2.