Synthesis of a Nonionic Polymer Surfactant from Cyclic Imino Ethers by the Terminator Method

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ABSTRACT: A nonionic polymer surfactant having a hydrophilic poly(*N*-acylalkylenimine) segment has been synthesized from a cyclic imino ether monomer, in which a hydrophobic group was introduced by terminating the living end of the propagating polymer ("terminator method"). 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. The surfactant properties of the product polymers were evaluated by the surface tension (γ) of the aqueous polymer solution. Three kinds of terminator were employed: (i) With 2-(higher alkyl)- or 2-[3-(perfluorooctyl)propyl]-4,4-dimethyl-2-oxazoline having reduced polymerizability, the living end of the propagating polymer was terminated, followed by hydrolysis to give the nonionic polymer surfactant having a higher alkyl or 3-(perfluorooctyl)propyl group. (ii) 2-*n*-Octyl- or 2-*n*-undecyl-5-methyl-2-oxazoline was used as the terminator in a similar method. (iii) With a primary or secondary (higher alkyl)amine and (perfluoroheptyl)methylamine, the living end of the polymer was terminated, followed by deionization to produce the polymer surfactant. Using a primary (higher alkyl)amine or (perfluoroheptyl)methylamine gave a versatile method for producing effective nonionic polymer surfactants. The lowest γ value via (iii) reached 19.5 dyn/cm for a polymer sample from 2-methyl-2-oxazoline monomer/(perfluoroheptyl)methylamine terminator.

Introduction

Cationic ring-opening polymerization of cyclic imino ethers provides 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 a poly(*N*-acylethylenimine) becomes hydrophilic or hydrophobic by changing the nature of the acyl group. Recently we have paid attention to this property and synthesized two types of new nonionic polymer surfactants by utilizing the living nature of the cationic polymerization of cyclic imino ethers.[2,3] One is a block copolymer from cyclic imino ethers; AB and ABA (or BAB) type block copolymers, in which A and B denote hydrophilic and hydrophobic polymer chains, respectively, were prepared by one-pot two-stage or one-pot three-stage copolymerizations.[2] These copolymers possess both hydrophilic and hydrophobic chains in the same molecule and, hence, showed very good surfactant properties evaluated by the surface tension (γ) of copolymer in water. The other is a nonionic polymer surfactant having a hydrophilic poly(*N*-acylalkylenimine) segment and a hydrophobic group, in which the latter group was introduced at the initiation stage of polymerization of the monomer ("initiator method").[3,4] The present paper deals with the synthesis of another type of a nonionic polymer surfactant by terminating the living end of the propagating polymer with a nucleophile having a hydrophobic group ("terminator method"). To construct a hydrophilic polymer segment, the 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). As terminators providing a hydrophobic group, the nucleophiles employed are 2-(higher alkyl)- and 2-[3-(perfluorooctyl)-propyl]-2-oxazolines having a reduced polymerizability and primary and secondary (higher alkyl)amines and (perfluoroheptyl)methylamine.

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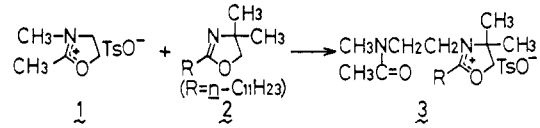
Results and Discussion

4,4-Dimethyl-2-substituted-2-oxazolines as Terminator. It is well-known that 4,4-dimethyl-2-substituted-2-oxazolines have a reduced polymerizability,[1b] and hence, they are expected to react with the living ends of propagating polymers from 2-oxazoline monomers. Therefore a model reaction was carried out to examine the reactivity of 2-alkyl-4,4-dimethyl-2-oxazoline **2** with the living end of poly(*N*-acylalkylenimine), in which 2,3-dimethyl-2-oxazolinium tosylate (**1**) is a model compound for the living end. The reaction was performed in acetonitrile at 120 °C for 10 h. In the gel permeation chromatography (GPC) chart after the reaction, a peak of the starting substrate **1** disappeared and a new, single peak appeared, which implies that the expected compound **3** is quantitatively formed. The structure of **3** was confirmed by ^{1}H NMR and IR spectra.



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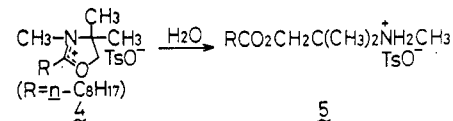
Another model reaction was carried out to examine the structure of the hydrolysis product of the terminal oxazolinium salt, in which 2-*n*-octyl-3,4,4-trimethyl-2-oxazolinium tosylate (**4**) is a model compound for **3**. The



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reaction was monitored by ^{1}H NMR in D_2O (Figure 1). The peak at 4.6 ppm (OCH_2C in **4**) gradually disappeared and a new peak at 4.0 ppm due to CO_2CH_2 of **5** appeared. Then, after 2 h the former changed completely to the latter. It is known that the hydrolysis product possesses an amide–alcohol structure in the case of

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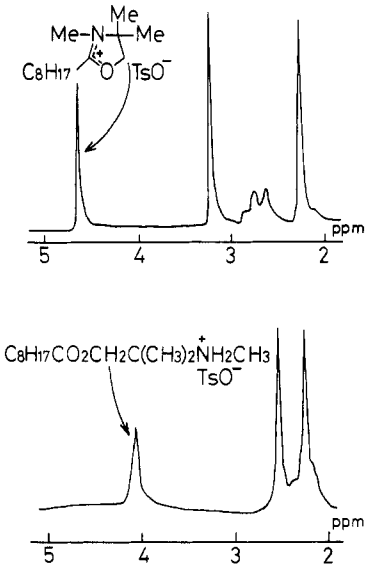
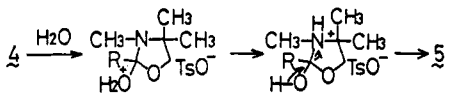
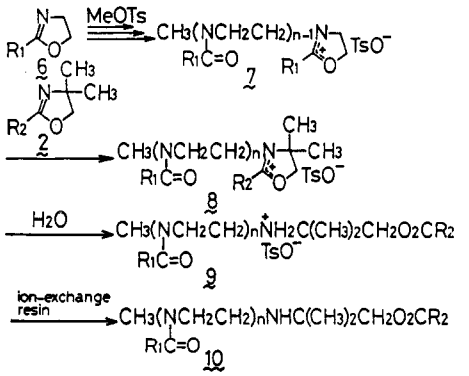


Figure 1. 60-MHz ^{1}H NMR spectrum before (upper) and after (lower) hydrolysis of 2-*n*-octyl-3,4,4-trimethyl-2-oxazolinium tosylate (**4**).

hydrolysis of 2-oxazolinium salt in water.[5,6] However, the IR spectrum of the hydrolysis product of **4** (after deionization) showed no characteristic peak at 1620 cm^{-1} due to an amide group but the characteristic peak at 1740 cm^{-1} due to an ester group, indicating that the hydrolysis product possesses the ester–amine structure **5**. The structure of **5** was also confirmed by ^{1}H and ^{13}C NMR. The reaction mechanism is given as follows.[5,6]



The polymerization of MeOZO or EtOZO **6** was carried out using methyl tosylate (MeOTs) as initiator in acetonitrile at 60 °C. The living end of polymer **7** was allowed to react with 4,4-dimethyl-2-substituted-2-oxazoline **2** at 120 °C for 20 h to produce polymer **8** having the oxazolinium group at the terminal. **8** was easily hydrolyzed in water to give an amine–ester type product **9** as indicated in the model reaction shown. Then, **9** was deionized by an ion-exchange resin to product **10**. 2-



(Higher alkyl)-4,4-dimethyl-2-oxazolines reacted quantitatively with the living ends of polymer **7** to give **8**. However, 4,4-dimethyl-2-perfluoroalkyl-2-oxazoline as a terminator did not react quantitatively with **7** under similar reaction conditions due to a reduced nucleophilic reactivity of the fluorine-containing terminator. The molecular weight distribution of **10** evaluated as M_w/M_n was

Table I
Synthesis of Polymer Surfactant from 2-Oxazolines (6) with 4,4-Dimethyl-2-substituted-2-oxazoline Terminators

	polymerization[a]				characterization	
entry	R_1	R_2	n[b]	yield, %	γ of **9**,[c] dyn/cm	γ of **10**,[c] dyn/cm
1	Me	*n*-C_8H_{17}	2.9	100	34 5	33.2
2	Me	*n*-$C_{11}H_{23}$	2.9	82	38.2	32.2
3	Me	*n*-$C_{14}H_{29}$	3.2	99	38.7	32.4
4	Me	*n*-C_5H_{11}	6.0	98	55.9	40.6
5	Me	*n*-C_8H_{17}	6.0	100	34.8	38.7
6	Me	*n*-$C_{11}H_{23}$	5.8	88	40.8	36.0
7	Me	*n*-$C_{14}H_{29}$	5.8	89	41.1	40.3
8	Me	*n*-C_8H_{17}	9.0	100	46.0	39.0
9	Me	*n*-$C_{11}H_{23}$	9.0	98	43.7	36.7
10	Me	*n*-$C_{14}H_{29}$	8.9	94	45.0	41.5
11	Me	*n*-$C_8F_{17}(CH_2)_3$	3.1	73	23.5	19.1
12	Me	*n*-$C_8F_{17}(CH_2)_3$	5.9	88	27.5	21.4
13	Et	*n*-C_5H_{11}	3.0	93	50.0	42.7
14	Et	*n*-C_8H_{17}	3.0	87	32.7	31.9
15	Et	*n*-$C_{11}H_{23}$	3.1	58	36.7	31.6
16	Et	*n*-$C_{14}H_{29}$	3.1	95	37.3	32.7
17	Et	*n*-C_5H_{11}	6.0	100	52.7	42.7
18	Et	*n*-C_8H_{17}	6.0	93	33.4	37.7
19	Et	*n*-$C_{11}H_{23}$	5.8	95	38.2	35.2
20	Et	*n*-$C_{14}H_{29}$	5.9	90	38.5	39.9
21	Et	*n*-C_8H_{17}	9.0	100	37.7	37.9
22	Et	*n*-$C_{11}H_{23}$	9.0	97	41.9	35.8
23	Et	*n*-$C_{14}H_{29}$	9.0	91	41.9	40.0
24	Et	*n*-$C_8F_{17}(CH_2)_3$	3.0	53	20.6	17.7
25	Et	*n*-$C_8F_{17}(CH_2)_3$	6.0	65	27.8	24.4
26	Et	*n*-$C_8F_{17}(CH_2)_3$	8.9	72	29.1	25.0

[a] Polymerization was carried out at 60 °C under nitrogen. [b] Calculated from the monomer to initiator ratio. [c] The surface tension (γ) 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.

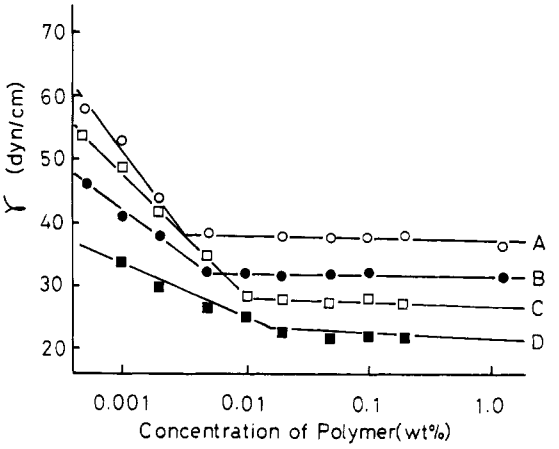


Figure 2. Polymer concentration–γ relationships: (A) **9** of entry 3; (B) **10** of entry 3; (C) **9** of entry 12; (D) **10** of entry 12.

calculated: 1.14, 1.10, 1.20, and 1.27 for entries 1, 2, 10, and 12 of Table I, respectively.

The polymerization results are given in Table I. As an indication of the surfactant nature, the surface tension (γ) was measured in water. The γ values were obtained with aqueous polymer solutions of 1.0 wt %, which was higher than the critical micelle concentration (cmc), <0.01 wt %, as shown in Figure 2. Surface activities reflected by γ values depend upon the nature of R_1 and R_2 as well as the degree of polymerization (DP) of 2-oxazoline monomers. With fixing R_1 as ethyl group and the chain length $n \sim 3$ or ~ 6, the nature of the lipophilic group is examined as a function of carbon number of the alkyl group with γ values (entries 13–20). In the case of

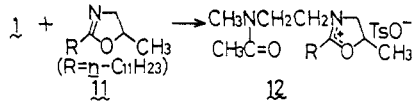
Table II
Synthesis of Polymer Surfactant from 2-Oxazolines (6) with 5-Methyl-2-substituted-2-oxazolines

entry	polymerization[a] R_1	R_2	n[b]	yield, %	characterization: γ,[c] dyn/cm
27	Me	n-C_8H_{17}	3.2	92	29.6[d]
28	Me	n-$C_{11}H_{23}$	3.2	100	35.2[d]
29	Me	n-C_8H_{17}	6.2	96	29.8
30	Me	n-$C_{11}H_{23}$	6.2	97	35.1
31	Me	n-C_8H_{17}	9.0	99	31.2[d]
32	Me	n-$C_{11}H_{23}$	9.0	100	38.7
33	Et	n-C_8H_{17}	5.7	92	29.2
34	Et	n-$C_{11}H_{23}$	5.7	88	35.7
35	MeOZI[e]	n-$C_{11}H_{23}$	5.9	96	35.8

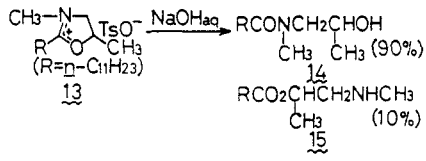
[a] Polymerization was carried out at 80 °C under nitrogen. [b] Calculated from the monomer to initiator ratio. [c] The value of the polymer mixture of **16** and **17** determined in a similar manner as those in Table I. [d] Measured with the concentration = 0.5 wt %. [e] 2-Methyl-5,6-dihydro-4*H*-1,3-oxazine was used as the monomer.

ionic polymer **9**, the *n*-octyl group was the most suitable among R_2 groups examined. On the other hand, the *n*-undecyl group was the most suitable in the case of nonionic polymer **10** and the change of γ values was smaller than that of **9**. As a whole, the longer chain length in polymers **9** and **10** decreases the surfactant properties. The chain length $n \sim 3$ seemed the most suitable. The longer the chain length among n examined ($n \sim 3$–9), the higher the γ value. Samples using a perfluoroalkyl group in R_2 especially showed good surfactant properties; for example, polymers **10** of entry 11 and 24 exhibit a value lower than 20 dyn/cm.

5-Methyl-2-substituted-2-oxazoline as Terminator. It is known that 2,5-dimethyl-2-oxazoline has little ability to polymerize.[7] Therefore, 2-(higher alkyl)-5-methyl-2-oxazoline can be used as a terminator of the living end **7**. A model reaction was carried out to examine the reactivity of 5-methyl-2-*n*-undecyl-2-oxazoline (**11**) toward **7**, in which 2,3-dimethyl-2-oxazolinium tosylate (**1**) is a model compound of the living species **7**. The model reaction was performed in acetonitrile at 120 °C for 10 h. In the GPC charts, the peak of **1** disappeared after the reaction and instead a new, single peak appeared, indicating that the expected compound **12** was quantitatively formed. The structure of **12** was confirmed from ^{1}H NMR and IR spectra.



Another model reaction was carried out to examine the structure of the hydrolysis product of the terminal oxazolinium salt, where 3,5-dimethyl-2-*n*-undecyl-2-oxazolinium tosylate (**13**) is a model compound. **13** was hydrolyzed in 1 N NaOH aqueous solution to give a mixture of **14** having an amide–alcohol structure and **15** having an ester–amine structure. The content of **14** and **15** was calculated from ^{1}H as well as ^{13}C NMR analysis as 90 and 10%, respectively.



The polymerization of 2-oxazolines **6** and the termination of **7** with **11** were performed similarly. Terminators

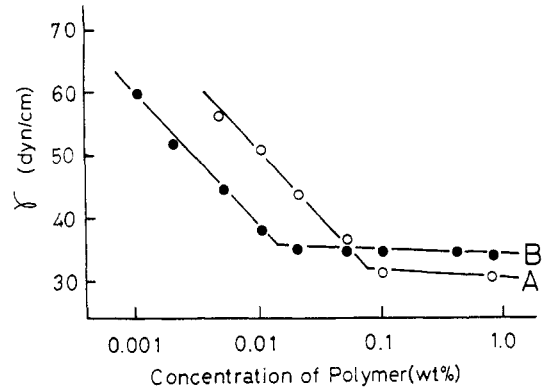
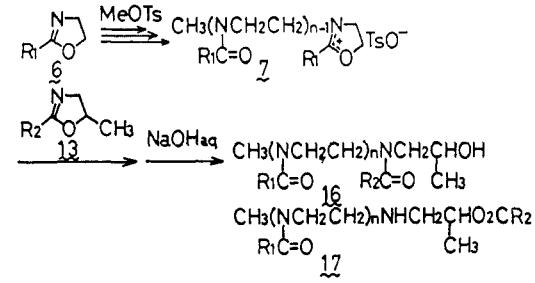


Figure 3. Polymer concentration–γ relationship: (A) polymer sample of entry 31; (B) polymer sample of entry 34.

used for construction of the hydrophobic group are 5-methyl-2-*n*-octyl-2-oxazoline and 5-methyl-2-*n*-undecyl-2-oxazoline. After the hydrolysis, the products **16** and **17** could not be separated. It was confirmed from ^{1}H NMR analysis that **11** was introduced at the terminus of **7** quantitatively. The molecular weight distribution evaluated by M_w/M_n was calculated: 1.26 and 1.15 for entries 34 and 35, respectively. The surface tension of the mixture of **16** and **17** was examined (Table II). All polymers showed excellent surface properties. Figure 3 indicates the γ value dependency with respect to the polymer concentration. The cmc values of both samples of entry 31 and 34 are lower than 0.1 wt %.



Primary and Secondary Amines as Terminator. Many primary and secondary (higher alkyl)amines are commercially available, and hence, using them as terminator is the most versatile manner to introduce the hydrophobic group into the living end **7**. A primary or secondary amine was added to **7** to give the polymer **18** having an ammonium group at the end, followed by deionization to produce the nonionic polymer surfactant **19** (Table III). It was confirmed by ^{1}H NMR that alkylamines were introduced at the terminal **7** quantitatively. However, a perfluoroalkylamine terminator was not quantitatively introduced at the terminal, which was due to the lack of the nucleophilicity of the perfluoroalkylamine (entries 49–51). The M_w/M_n values obtained by gel permeation chromatography (GPC) were as follows: entry 46, 1.29; entry 47, 1.11; entry 48, 1.40; entry 50, 1.30; entry 57, 1.14; entry 62, 1.21.

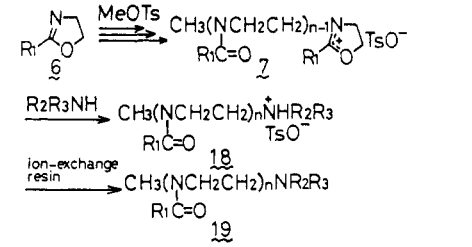


Table III
Synthesis of Polymer Surfactant from 2-Oxazolines (6) with Primary and Secondary Amines as Terminator

	polymerization[a]				characterization:
entry	R_1	amine	n^b	yield, %	γ of 19,[c] dyn/cm
36	Me	n-$C_4H_9NH_2$	3.0	100	34.9
37	Me	n-$C_8H_{17}NH_2$	3.1	95	27.2
38	Me	n-$C_{12}H_{25}NH_2$	3.0	100	22.0
39	Me	n-$C_{16}H_{33}NH_2$	3.0	89	27.6[d]
40	Me	n-$C_4H_9NH_2$	6.0	100	37.0
41	Me	n-$C_8H_{17}NH_2$	5.8	100	28.5
42	Me	n-$C_{12}H_{25}NH_2$	5.9	100	23.0
43	Me	n-$C_{16}H_{33}NH_2$	5.8	90	28.0[d]
44	Me	n-$C_4H_9NH_2$	9.3	96	38.4
45	Me	n-$C_8H_{17}NH_2$	9.1	98	29.9
46	Me	n-$C_{12}H_{25}NH_2$	8.8	100	23.8
47	Me	n-$C_{16}H_{33}NH_2$	8.9	96	26.8[d]
48	Me	n-$C_{12}H_{25}NH_2$	19.1	98	26.8
49	Me	n-$C_7F_{15}CH_2NH_2$	3.0	66	19.5
50	Me	n-$C_7F_{15}CH_2NH_2$	5.9	64	28.8
51	Me	n-$C_7F_{15}CH_2NH_2$	9.0	66	33.0
52	Me	n-$C_4H_9NHCH_3$	6.5	96	34.7
53	Me	$(n$-$C_4H_9)_2NH$	5.8	94	42.2
54	Me	$(n$-$C_6H_{13})_2NH$	6.4	91	30.0
55	Me	$(n$-$C_8H_{17})_2NH$	6.6	94	30.5
56	Et	n-$C_{12}H_{25}NH_2$	2.9	95	22.4[d]
57	Et	n-$C_4H_9NH_2$	5.7	89	36.7
58	Et	n-$C_8H_{17}NH_2$	5.6	100	28.0
59	Et	n-$C_{12}H_{25}NH_2$	5.7	96	23.0
60	Et	n-$C_{16}H_{33}NH_2$	5.9	85	27.6[d]
61	Et	n-$C_{12}H_{25}NH_2$	9.1	94	24.5
62	MeOZI[e]	n-$C_{12}H_{25}NH_2$	5.9	91	25.8[d]

[a] Polymerization was carried out at 60 °C under nitrogen. [b] Calculated from the monomer to initiator ratio. [c] Determined in a similar way as those in Table I. [d] Measured with the concentration = 0.5 wt %. [e] 2-Methyl-5,6-dihydro-4*H*-1,3-oxazine was used as the monomer.

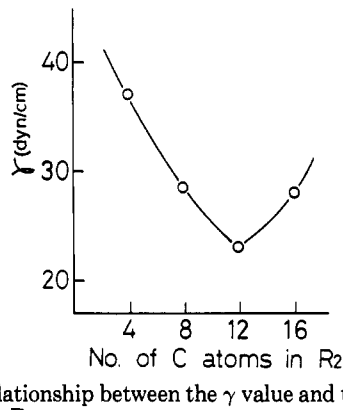


Figure 4. Relationship between the γ value and the chain length of alkyl group R_2.

With R_1 fixed as a methyl group and the chain length fixed as $n \sim 6$ (entries 40–43), the nature of the lipophilic group in primary amines is examined as a function of the carbon number of the alkyl group R_2 with γ values (Figure 4). The n-dodecyl group was found the most suitable. A similar tendency was observed for $n \sim 3$ (entries 36–39) and $n \sim 9$ (entries 44–47). For the polymer samples with n-dodecylamine terminator, the γ value did not vary essentially with n = 3.0, 5.9, and 8.8 and slightly increased with n = 19.1 (entry 38, 42, 46, and 48). With secondary amines as the terminator, γ values were higher than those with primary higher alkylamines. The γ value was lower than 20 dyn/cm with a perfluoroalkyl amine terminator (entry 49).

Surface tensions of four samples **19** are plotted as a function of the polymer concentration in Figure 5. The cmc values were smaller than 0.5 wt % in all cases. In using secondary amines and perfluoroalkyl amine as a terminator, the cmc of **19** was lower than that from a primary amine terminator.

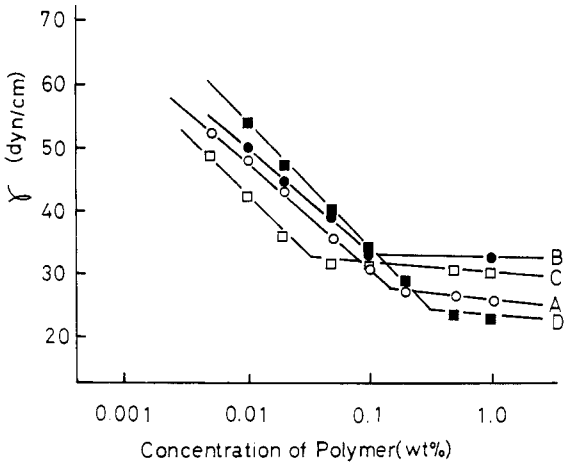


Figure 5. Polymer concentration–γ relationships: (A) polymer sample of entry 43; (B) polymer sample of entry 51; (C) polymer sample of entry 55; (D) polymer sample of entry 59.

Experimental Section

Materials. Solvents, acetonitrile, n-hexane, diethyl ether, and THF were purified in a usual manner. Commercial reagents of MeOTs, MeOZO, n-butylamine, n-octylamine, n-dodecylamine, n-cetylamine, N-methyl-n-butylamine, di-n-butylamine, di-n-hexylamine, and di-n-octylamine were purified by distillation. EtOZO, a gift from Dow Chemical Co., was also purified by distillation. MeOZI was prepared according to the literature.[8] 2-(Perfluorooctyl)ethyl iodide was supplied from Daikin Ind. Co. and used without further purification. (Perfluoroheptyl)methylamine (PCR Inc.) was used without purification. 2,3-Dimethyl-2-oxazolinium tosylate was prepared according to the literature.[9] All distillations were carried out under nitrogen.

Preparation of 4,4-Dimethyl-2-*n*-octyl-2-oxazoline (2).[8] A mixture of n-octyl cyanide (13.94 g, 100 mmol), 2-amino-2-methyl-2-propanol (8.91 g, 100 mmol), and zinc chloride (0.34 g, 2.5 mmol) was heated at 130 °C for 23 h. The mixture was distilled to give 18.81 g of 4,4-dimethyl-2-n-octyl-2-oxazoline (**2**) (yield 89%): bp 93 °C (1.0 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 6.0 Hz, CH_3C, 3 H), 1.1–1.6 (m, CCH_2C, 12 H), 1.4 (s, CH_3C, 6 H), 2.2 (t, J = 6.0 Hz, CCH_2C, 2 H), 3.9 (s, CCH_2O, 2 H); IR (neat) 1670 cm^{-1} ($\nu_{C=N}$).

Preparation of 4,4-Dimethyl-2-[3-(perfluorooctyl)propyl]-2-oxazoline (2).[10] To a solution containing 2.0 g (17.7 mmol) of 2,4,4-trimethyl-2-oxazoline in 30 mL of THF was added an n-butyl lithium solution (16.8 mmol) dropwise at −78 °C and the mixture was allowed to react at −78 °C for 30 min. To this mixture, 9.6 g (16.8 mmol) of 2-(perfluorooctyl)ethyl iodide in 15 mL of THF was added dropwise. Then, the mixture was poured into a saturated NaCl solution (100 mL) and extracted three times with 30 mL of diethyl ether. The organic layer was separated and dried over $MgSO_4$ for 1 h, followed by evaporation, and the residue was subjected to separation by using a silica gel column with diethyl ether and pentane to give 4.16 g of 4,4-dimethyl-2-[3-(perfluorooctyl)propyl]-2-oxazoline (**2**) (42% yield): ^{1}H NMR ($CDCl_3$) δ 1.3 (s, CH_3C, 3 H), 1.7–2.8 (m, CCH_2C, 6 H), 3.9 (s, CCH_2O, 2 H).

Preparation of 2-*n*-Octyl-3,4,4-trimethyl-2-oxazolinium Tosylate (4). To a diethyl ether solution (2 mL) containing 4.01 g (3.13 mmol) of MeOTs was added 1.71 g (8.07 mmol) of 4,4-dimethyl-2-n-octyl-2-oxazoline and the mixture was stirred at 30 °C for 3 h. Diethyl ether (20 mL) was added to the mixture to precipitate white solids, followed by filtration to give 3,4,4-trimethyl-2-n-octyl-2-oxazolinium tosylate (**4**): ^{1}H NMR ($CDCl_3$) δ 0.8 (t, J = 5.0 Hz, CH_3C, 3 H), 1.0–1.7 (m, CCH_2C, 12 H), 1.4 (s, CH_3C, 6 H), 2.3 (s, CH_3–Ar, 3 H), 2.7 (q, J = 7.0 Hz, CCH_2C, 2 H), 3.2 (s, CH_3N, 3 H), 4.6 (s, CCH_2O, 2 H), 7.0 and 7.6 (two d, J = 9.0 Hz, $CC_6H_4SO_3$, 4 H).

Reaction of 2,3-Dimethyl-2-oxazolinium Tosylate (1) with 4,4-Dimethyl-2-*n*-undecyl-2-oxazoline (2). In a glass tube,

0.42 g (1.5 mmol) of 2,3-dimethyl-2-oxazolinium tosylate (1) was dissolved in 3 mL of acetonitrile, and 0.47 g (1.9 mmol) of 4,4-dimethyl-2-*n*-undecyl-2-oxazoline (**2**) was added under nitrogen. The tube was sealed and kept at 120 °C for 10 h. Then the tube was opened and the solvent was evaporated. The residue was dissolved in 3 mL of chloroform and poured into 70 mL of *n*-hexane to precipitate pale yellow materials, followed by filtration to give 0.76 g of 3-(2-(*N*-acetyl-*N*-methylamino)-ethyl)-4,4-dimethyl-2-*n*-undecyl-2-oxazolinium tosylate (**3**) (yield 97%): ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 4.0 Hz, CH_3C, 3 H), 1.1–1.5 (m, CCH_2C, 18 H), 1.6 (s, CH_3C, 6 H), 2.0 (s, $CH_3C{=}O$, 3 H), 2.3 (s, CH_3–Ar, 3 H), 2.9–3.1 (m, CCH_2C, 2 H), 3.1 (s, CH_3N, 3 H), 3.5–4.1 (m, CCH_2C, 4 H), 4.7 (s, CCH_2O, 2 H), 7.2 and 7.7 (two d, J = 8.0 Hz, $CC_6H_4SO_3$, 4 H); IR (neat) 1740 ($\nu_{C=N}$), 1620 cm^{-1} ($\nu_{C=O}$).

Similarly, **reaction of 2,3-dimethyl-2-oxazolinium tosylate (1) with 5-methyl-2-*n*-undecyl-2-oxazoline (11)** afforded 3-[2-(*N*-acetyl-*N*-methylamino)ethyl]-5-methyl-2-*n*-undecyl-2-oxazolinium tosylate (**12**) in 53% yield: ^{1}H NMR ($CDCl_3$) δ 0.8–1.8 (m, CH_3C and CCH_2C, 24 H), 2.0, (s, $CH_3C{=}O$, 3 H), 2.3 (s, CH_3–Ar, 3 H), 2.7–3.0 (m, CCH_2C, 2 H), 3.0 (s, CH_3N, 3 H), 3.5–4.2 (m, CCH_2N, 4 H), 5.2–5.5 (m, CCH_2O, 1 H), 7.1 and 7.7 (two d, J = 9.0 Hz, $OC_6H_4SO_3$, 4 H); IR (neat) 1740 ($\nu_{C=N}$), 1630 cm^{-1} ($\nu_{C=O}$).

Hydrolysis of 2-*n*-Octyl-3,4,4-trimethyl-2-oxazolinium Tosylate (4). 2-*n*-Octyl-3,4,4-trimethyl-2-oxazolinium tosylate (4) was dissolved in water and stood overnight. To the mixture was added ion-exchange resin (DIAION A 21) and this was stirred for 6 h. After filtration of the ion-exchange resin, the filtrate was extracted with diethyl ether. The organic layer was separated and dried over $MgSO_4$, followed by evaporation to give 2-(*N*-methylamino)-2-propyl nonanoate: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 5.0 Hz, CH_3C, 3 H), 1.1 (s, CH_3C, 6 H), 1.2–1.6 (m, CCH_2C, 12 H), 2.2–2.4 (m, $CCH_2C{=}O$, 2 H), 2.3 (s, CH_3N, 3 H), 4.0 (s, CCH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.0, 21.6, 24.7, 28.2, 30.8 (*n*-octyl, CH_3 and CH_2), 27.6 ($(CH_3)_2C$), 33.3 ($CH_2C{=}O$), 51.4 ($C(CH_3)_2$), 68.3 (OCH_2), 172.7 (C=O); IR (neat) 1740 cm^{-1} ($\nu_{C=O}$).

Similarly, **hydrolysis of 5-methyl-2-*n*-undecyl-2-oxazolinium tosylate (13)** by 1 N NaOH afforded a mixture of **14** and **15**. The content of **14** and **15** was 90 and 10%, respectively: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 4.0 Hz, CH_3C, 3 H), 1.0–1.6 (m, CH_3C and CCH_2C, 21 H), 2.1–2.5 (m, $CH_2C{=}O$, 2 H), 2.3 (**15**) (s, CH_3N, 3 H), 3.0 (**14**) (s, CH_3N, 3 H), 3.1–3.5 (m, CCH_2N, 2 H), 4.5–4.8 (m, CCHO, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.4, 24.7, 25.2, 25.6, 29.3, 31.6 (*n*-undecyl, CH_3 and CH_2), 20.5 (**15**) (CH_3CH), 20.9 (**14**) (CH_3CH), 33.0, 34.0, 36.4, 37.2 (**14**) ($CH_2C{=}O$ and CH_3N), 33.3 (**15**) ($CH_2C{=}O$), 46.8 (**15**) (CH_3N), 55.9, 56.1 (**14**) (CH_2N), 57.2 (**15**) (CH_2N), 64.9 (**15**) ($OCHCH_3$), 66.7 (**14**) ($OCHCH_3$), 174.1, 174.3, 174.9 (C=O); IR (neat) 1730 (**15**) ($\nu_{C=O}$), 1630 cm^{-1} (**14**) ($\nu_{C=O}$).

Polymerization Using 4,4-Dimethyl-2-substituted-2-oxazoline as Terminator. A typical run was as follows (entry 18). In a glass tube, 0.610 g (6.16 mmol) of EtOZO and 0.190 g (1.02 mmol) of MeOTs were dissolved in 3 mL of acetonitrile under nitrogen. The tube was sealed and kept at 60 °C for 14 h. The tube was opened and 0.311 g (1.05 mmol) of 4,4-dimethyl-2-*n*-octyl-2-oxazoline was added to the mixture. The tube was sealed again and kept at 120 °C. After 20 h, the tube was opened. The solvent was evaporated and the residue was dissolved into 2 mL of chloroform. The mixture was poured into 80 mL of *n*-hexane to precipitate the polymer materials, followed by filtration to give 0.95 g of **8** (yield 93%). **8** was dissolved in 20 mL of water and the mixture stood for 4 h. To the mixture was added ion-exchange resin (DIAION A 21) and stirred overnight. After filtration the filtrate was extracted with chloroform (30 mL × 3). The organic layer was separated and dried over $MgSO_4$, followed by evaporation to give **10** quantitatively: ^{1}H NMR ($CDCl_3$) δ 0.8–1.5 (m, CH_3C and CCH_2C), 2.0–2.6 (br, $CH_2C{=}O$), 2.7 (m, CH_2N), 3.0 (s, CH_3N), 3.2–3.7 (CCH_2N), 3.9 (s, CH_2O).

Similarly, the polymerization using 4,4-dimethyl-2-[3-(perfluorooctyl)propyl]-2-oxazoline **2** as terminator afforded **10** (yield 88% for entry 12). From the elemental analysis (the ratio of C and F content), 75% of the living end of **7** reacted with **2**.

Polymerization Using 5-Methyl-2-substituted-2-oxazoline as Terminator. A typical run was as follows (entries 31 and 32). In a glass tube, 1.12 g (13.2 mmol) of MeOZO and 0.271 g (1.46 mmol) of MeOTs were dissolved in 4 mL of acetonitrile under nitrogen. The tube was sealed and kept at 80 °C for 9 h. Then, the tube was opened. The mixture was divided into two parts (2.34 and 2.12 g, respectively), which were transferred to two other glass tubes under nitrogen. To them were added 0.164 g (0.831 mmol) of 5-methyl-2-*n*-octyl-2-oxazoline (**11**) and 0.172 g (0.718 mmol) of 5-methyl-2-*n*-undecyl-2-oxazoline (**11**), respectively, and then the tubes were sealed and kept at 120 °C. After 20 h, the tubes were opened. After reprecipitation with acetonitrile as solvent and diethyl ether as nonsolvent, the polymeric materials were dissolved in 50 mL of 1 N NaOH aqueous solution and stirred for 1 h. The mixture was extracted with chloroform (30 mL × 3). The organic layer was separated and dried over $MgSO_4$. After evaporation of solvent and reprecipitation (chloroform–*n*-hexane), the polymeric materials were collected and dried in vacuo to give 0.69 g (99% yield, entry 31) and 0.68 g (100% yield, entry 32) of the mixture of **16** and **17**: ^{1}H NMR (entry 31, $CDCl_3$) δ 0.9 (t, J = 4.0 Hz, CH_3C), 1.0–1.7 (m, CH_3C and CCH_2C), 2.0 (s, $CH_3C{=}O$), 2.1–2.4 (m, $CH_2C{=}O$), 2.9–3.8 (br, CCH_2N), 4.2–4.5 (m, CCHO); IR (entry 31, neat) 1730 ($\nu_{OC=O}$), 1630 cm^{-1} ($\nu_{NC=O}$). Anal. Calcd for $C_{49.0}H_{90.0}N_{10.0}O_{11.0}(H_2O)_{2.0}$ (hygroscopic) (entry 31): C, 57.07; H, 9.19; N, 13.58. Found: C, 57.34; H, 9.18; N, 13.38. Anal. Calcd for $C_{52.0}H_{96.0}N_{10.0}O_{11.0}$ (entry 32): C, 60.21; H, 9.33; N, 13.50. Found: C, 60.34; H, 9.96; N, 13.05.

Polymerization Using Primary or Secondary Amine as Terminator. A typical run was as follows (entry 45). A mixture of 0.987 g (11.6 mmol) of MeOZO and 0.236 g (1.27 mmol) of MeOTs was dissolved in 3 mL of chloroform and the mixture was heated at 60 °C for 19 h under nitrogen. After cooling to 0 °C, 0.181 g (1.4 mmol) of *n*-octylamine was added and the mixture was stirred overnight. After reprecipitation (chloroform–*n*-hexane), the polymeric material was dissolved in acetonitrile. The solution was passed through an ion-exchange resin (Amberlyst A-21) and was evaporated. After reprecipitation (chloroform–*n*-hexane), the polymeric materials were collected and dried in vacuo to give 0.959 g (100% yield) of **19**: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 4.0 Hz, CH_3C), 1.0–1.4 (m, CCH_2C), 2.0 (s, $CH_3C{=}O$), 2.3–2.5 (m, CCH_2N), 2.7–4.0 (br, CCH_2N), 3.0 (s, CH_3N), 4.7–5.1 (br, NH).

Similarly, the polymerization using (perfluoroheptyl)methylamine as terminator afforded **19** (yield 66% for entry 49). From the elemental analysis (the ratio of C and F content), 49% of the living end **7** reacted with (perfluoroheptyl)methylamine.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a 60-MHz Hitachi R-600 NMR spectrometer and a 22.6-MHz Hitachi R-900 spectrometer, respectively. IR spectra were recorded on a Hitachi 260-50 spectrometer. Gel permeation chromatographic (GPC) analysis was performed by using JASCO TRIROTOR with RI and UV detectors under the following conditions: JSP-101 or Shodex K-802 or AC-803 column with chloroform eluent at a flow rate 1.0 or 0.5 mL/min. The surface tension (γ) of the aqueous polymer solutions was measured by a Shimadzu Du Noüy tensiometer at ambient temperature and the γ values obtained were recalculated to the values at 25 °C.

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Cationic Copolymerizations of Cyclooxaalkanes

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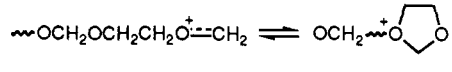
ABSTRACT: Cationic copolymerizations of 2-butyl-1,3-dioxepane (= 2-Bu-DOP) with 1,3-dioxolane (= DOL) and with tetrahydrofuran (= THF) have been carried out. The copolymers have T_g's in accordance with the Fox relationship. The reactivity ratios have been obtained by using Fineman–Ross analysis. The rate constants for 2-Bu-DOP (= a) and DOL (= b) copolymerization at −10 °C are $k_{a,a} = 7.1 \times 10^{-4}$, $k_{b,a} = 6.5 \times 10^{-4}$, $k_{ab} = 3.3 \times 10^{-4}$, and $k_{b,a} = 5.4 \times 10^{-4}$ in units of $(M\ s)^{-1}$; the corresponding rate constant values at 0 °C for the copolymerization of THF (= b) are 3.0×10^{-3}, 8.2×10^{-5}, 9×10^{-4}, and 7.4×10^{-4} $(M\ s)^{-1}$. The mechanisms of the copolymerizations are discussed.

Introduction

In the polymerization of oxygen heterocyclic compounds, the oxonium structure for the propagating species is widely accepted, i.e. in the case of tetrahydrofuran (= THF).[1] For 1,3-dioxaalkanes, the acetal bond is highly reactive and is easily opened in the presence of acid catalysts.[2] The ΔG_p of cyclic acetal polymerization has small negative or even positive value due to relatively low negative ΔH_p; consequently the monomer and polymer are in reversible equilibrium.[3] Thermodynamic parameters for polymerizations of DOL[3,4] (= 1,3-dioxolane), 4-Me-DOL,[5] DOP[3,4] (= 1,3-dioxepane), 4-Me-DOP,[6,7] 2-Me-DOP,[6,7] TOC[4b,8,9] (= 1,3,6-trioxocane), and 2-Bu-TOC have been reported. Because of the stabilizing effect of the α-oxygen atom, alkoxycarbenium, C^+, ions are in equilibrium with the cyclic oxonium ion, O^+. This is illustrated for DOL



(1)

Either ionic species can participate in propagation.

Penczek et al.[1] have argued that in the case of DOL the O^+ ion is the dominant propagating species. The fact that 2- and 4-Me-DOL's[10] form only oligomers seem to be consistent with a steric effect in the O^+ mechanism. However, recent observations that 2-alkyl derivatives of DOP[7] and TOC[9] polymerize at the same or faster rates than the unsubstituted monomers suggest the intermediacy of alkoxy carbenium ions in propagation. The central objective of this work is to investigate the copolymerizations of THF and DOL, which are both thought to polymerize via the cyclic oxonium ion, with 2-Bu-DOP, which may involve an alkoxycarbenium ion as a propagating species.

Experimental Section

Materials. 2-Bu-DOP was prepared by the reaction of 1,4-butanediol and valeraldehyde[11] in the presence of a Dowex 50-X8-100 ion-exchange resin as previously described.[7] THF, DOL, triethylamine, methylene chloride, and 1,2-dichloroethane from Aldrich were purified by usual procedures. Boron trifluoride etherate was distilled immediately before use.

Copolymerizations. Copolymerization was carried out in a Schlenk tube equipped with a magnetic stir bar and fitted with a rubber septum. Tubes were flame-dried under vacuum and filled with purified nitrogen. A mixture of monomers dissolved in either methylene chloride or 1,2-dichloroethane was introduced by syringe and equilibrated at the thermostated reaction temperature followed by injection of the catalyst solution. The conversion versus polymerization time was followed by quenching aliquot with a precisely weighed excess amount of triethylamine. A known amount of tetralin was added as the GC standard, and the sample was diluted with solvent. The concentration of unreacted monomer in the mixture was analyzed with GC. The monomer concentrations were calculated from calibration curves previously determined for known mixtures of 2-Bu-DOP/DOL and of 2-Bu-DOP/THF. The copolymers were precipitated by addition of triethylamine, washed with aqueous methanol, and evacuated at 100 °C to yield the copolymers.

Methods. An Hewlett-Packard 5790A chromatograph was used for GC using an OV-101 silicone packed column. A Varian Associates XL-200 instrument was used for ^1H NMR. A Perkin-Elmer DSC-II system was used to determine T_g at a 20 °C/min heating rate.

Results

Time Conversion of Polymerizations. The homopolymerization time conversion curves at −10 °C are shown

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