Synthesis of a Nonionic Polymeric Surfactant from 2-Oxazolines Having a Carboxylate Component as the Hydrophobic Group

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Introduction

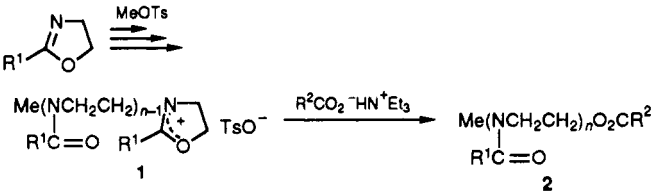
Electrophilic[1] (cationic) polymerization of 2-alkyl-2-oxazolines (ROZOs) is conveniently used to prepare poly(*N*-acylethylenimines) (PNAIs).[2] During the course of our studies on the polymerization of ROZOs, we have found that PNAI becomes hydrophilic or hydrophobic by changing the nature of the acyl group. Based on these observations, we recently synthesized three types of new nonionic polymeric surfactants by utilizing the living nature of the polymerization of 2-oxazolines.[3-5] One is a block copolymer from ROZOs; AB and ABA (or BAB) type block copolymers, in which A and B denote a hydrophilic and a hydrophobic chain, respectively, were synthesized by one-pot two-stage or one-pot three-stage processes. These copolymers possess both hydrophilic and hydrophobic chains in the same molecule and, hence, showed very good surfactant properties.[3] A second nonionic polymeric surfactant had a hydrophilic PNAI segment and a hydrophobic group, in which the latter group was introduced at the initiation stage of polymerization of 2-oxazolines ("initiator method")[4] or at the termination stage by reacting the living end of the propagating polymer with a hydrophobic amine ("terminator method").[5]

Very recently we have found that the living propagating species of PNAI reacted with a nucleophile from (meth)acrylic acid such as silver methacrylate and a mixture of (meth)acrylic acid and triethylamine to produce a (meth)acryl-type PNAI macromonomer, quantitatively; in the latter case, triethylammonium (meth)acrylate is probably a nucleophilic species.[6] On this basis, the present paper describes the synthesis of another type of nonionic polymer surfactant by the terminator method. A higher fatty acid is employed to provide a hydrophobic group, and a polymer chain from 2-methyl- or 2-ethyl-2-oxazoline is utilized as a hydrophilic segment. The nucleophile that terminates the living PNAI species is a mixture of the acid and triethylamine.

Results and Discussion

Synthesis of a Nonionic Surfactant of PNAI Having a Hydrophobic Group at One End. The polymerization of MeOZO or EtOZO was carried out in acetonitrile at 70 °C by using methyl tosylate (MeOTs) as a monofunctional initiator. The living propagating species **1** was reacted with a mixture of carboxylic acid and triethylamine at 70 °C for 48 h, followed by treatment with an ion-exchange resin to give the nonionic polymer surfactant **2** (Table I).

Figure 1 shows ^{1}H NMR spectrum of **2** (entry 3). Peak C is assigned to methyl protons derived from the initiator. Peak H is ascribed to the methyl protons of the higher fatty acid. The integrated areas of peaks C and H are almost equal. Furthermore, the ratio of the integrated



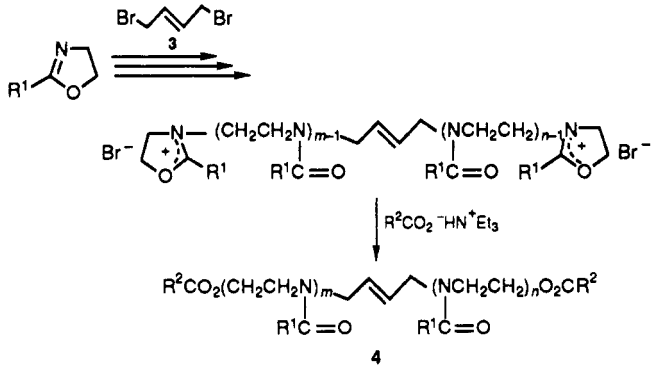
areas of peaks C and A, due to CC(=O)OCH$_2$C, was 3:2. These data indicate that the acid group was introduced quantitatively. Assignments for other peaks are given in Figure 1. The functionality, i.e., the number of higher fatty acid groups per molecular, was determined by ^{1}H NMR spectroscopy (Table I). The value is almost exactly 1.0, supporting the quantitative introduction of the acid group.

The degree of polymerization (DP) of **2** determined by ^{1}H NMR was always very close to the feed ratio of the initiator and monomer. The M_w/M_n values obtained by gel permeation chromatography (GPC) were very narrow: entry 3, 1.06; 5, 1.07; 13, 1.13. These data support the living nature of the polymerization of ROZO and that the termination reaction proceeds quantitatively.

The surface properties of **2** were evaluated by measuring the surface tension (γ) of **2** in water. Fixing R^1 as a methyl group and the chain length as $n \sim 11$, the nature of the hydrophobic group is examined as a function of carbon number of the alkyl (R^2) group with γ values (entries 5–9). The myristate group gave the lowest value of γ (entry 7). For the polymer samples with a lauric acid terminator, the γ value slightly increased with an increasing DP of **2** (entries 1, 3, 6, 11, and 12). It is to be noted that polymer samples with the oleate group showed better surfactant properties (lower γ) than those with the stearate group (entries 9, 10, 18, and 19). This is probably because oleate possesses an unsaturated carbon–carbon bond and hence is less hydrophobic than the stearate group. The two 2-oxazolines examined were efficient hydrophilic groups; the γ values for polymers having poly(EtOZO) chains are almost the same as those with poly(MeOZO) chains.

Figure 2 indicates the γ value dependency with respect to the polymer concentration. The longer the chain length in the hydrophobic group, the smaller the critical micelle concentration (cmc) value.

Synthesis of a Nonionic Surfactant of PNAI Having a Hydrophobic Group at Both Ends. Very recently we have found that an allylic dihalide, 1,4-dibromo-2-butene (**3**), is a bifunctional initiator for the polymeriza-



tion of 2-oxazolines, giving rise to a "fast initiation system" of living nature.[7] By using 1,4-dibromo-2-butene as an initiator, a hydrophobic group was introduced at both ends of PNAI in a similar method described above. The functionality of **4** obtained by ^{1}H NMR analysis is nearly

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Table I
Synthesis of a Nonionic Surfactant of PNAI Having a Hydrophobic Group at One End

	polymerization[a]			polymer 2			
entry	R^1	R^2	$[R^1OZO]_0/[MeOTs]_0$	yield, %	DP[b]	γ[c]	functionality[b]
1	Me	n-$C_{11}H_{23}$	2.7	73	3.1	31.9[d]	0.98
2	Me	n-C_7H_{15}	5.1	85	5.6	34.4[e]	0.98
3	Me	n-$C_{11}H_{23}$	5.1	79	6.0	34.8	1.02
4	Me	n-$C_{17}H_{35}$	5.1	79	5.6	41.7	1.00
5	Me	n-C_7H_{15}	10.5	70	11.5	37.8	0.97
6	Me	n-$C_{11}H_{23}$	10.5	74	11.5	35.4	0.99
7	Me	n-$C_{13}H_{27}$	10.3	80	10.8	34.3	0.96
8	Me	n-$C_{15}H_{31}$	10.3	84	10.8	37.9	0.95
9	Me	n-$C_{17}H_{35}$	10.5	69	11.5	42.2	1.01
10	Me	n-$C_8H_{17}CH{=}CH(CH_2)_7$	10.3	78	10.8	34.9	1.00
11	Me	n-$C_{11}H_{23}$	15.1	81	14.3	36.7	1.03
12	Me	n-$C_{11}H_{23}$	20.5	85	18.8	39.7	1.01
13	Me	n-$C_{17}H_{35}$	20.5	88	18.8	48.9	0.95
14	Et	n-C_7H_{15}	4.9	65	5.1	32.9[e]	0.97
15	Et	n-$C_{11}H_{23}$	5.4	74	5.8	31.4	0.99
16	Et	n-C_7H_{15}	10.1	60	10.7	38.6[e]	1.01
17	Et	n-$C_{11}H_{23}$	10.1	70	10.7	38.1	1.02
18	Et	n-$C_{17}H_{35}$	10.0	81	9.9	40.5	1.00
19	Et	n-$C_8H_{17}CH{=}CH(CH_2)_7$	10.0	72	9.9	38.1	1.04

[a] Polymerization was carried out at 70 °C under argon. [b] Determined from ^1H NMR analysis. [c] The surface tension was measured with a Du Noüy tensiometer with the polymer concentration = 0.5 wt %, which is higher than the critical micelle concentration at an ambient temperature and recalculated to the value at 25 °C. [d] Measured with the concentration = 0.2 wt %. [e] Measured with the concentration = 1.0 wt %.

Table II
Synthesis of a Nonionic Surfactant of PNAI Having a Hydrophobic Group at Both Ends

	polymerization[a]			polymer 4			
entry	R^1	R^2	$[ROZO]_0/[3]_0$	yield, %	DP[b]	γ[c]	functionality[b]
20	Me	n-C_7H_{15}	10.0	72	9.1	32.9[d]	1.97
21	Me	n-$C_{11}H_{23}$	10.0	73	9.1	33.2	2.06
22	Me	n-$C_{11}H_{23}$	19.6	83	19.2	37.1	1.96
23	Me	n-$C_{17}H_{35}$	19.6	82	19.2	42.6	1.99
24	Me	n-$C_8H_{17}CH{=}CH(CH_2)_7$	22.6	71	23.4	38.0	1.96
25	Et	n-$C_{11}H_{23}$	19.7	81	21.3	34.6	2.00

[a] Polymerization was carried out at 70 °C under argon. [b] Determined from ^1H NMR analysis. [c] Determined in a way similar to those in Table I. [d] Measured with the concentration = 1.0 wt %.

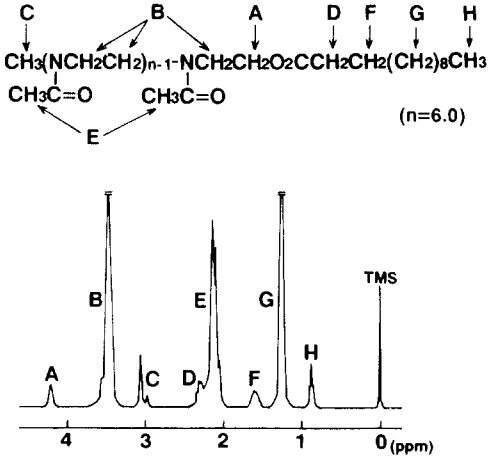

Figure 1. ^1H NMR spectrum of **2** in $CDCl_3$ (entry 3).

2.0 (Table II), indicating that the higher fatty acid group was introduced quantitatively at both ends of **4**. The DP value of 4 agreed well with the charged ratio. The molecular weight distribution evaluated by M_w/M_n was calculated: 1.08 and 1.09 for entries 20 and 22, respectively. These data can be taken to support that the polymerization of ROZO proceeded through a living system and the termination occurred quantitatively.

All samples were soluble in water and showed good surfactant properties. The shorter the chain length of PNAI segment, the lower the γ value.

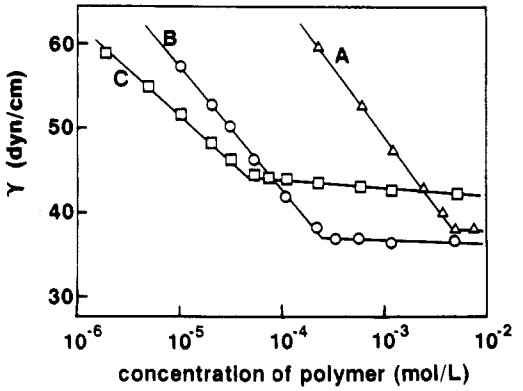

Figure 2. Relationships of the polymer concentration–the surface tension (γ): polymer samples of (A) entry 5, (B) entry 6, and (C) entry 9.

In conclusion, the present method allows the synthesis of new nonionic polymeric surfactants based on higher fatty acids coupled with PNAI segments as a hydrophilic group.

Experimental Section

Materials. Monomers MeOZO and EtOZO were purified by distillation over potassium hydroxide. Other reagents and solvents were purified by distillation or recrystallization. All operations were carried out under argon.

Synthesis of a Nonionic Surfactant of PNAI Having a Hydrophobic Group at One End. A typical run was as follows (entry 1). A mixture of 0.437 g (5.13 mmol) of MeOZO and 0.355

g (1.91 mmol) of MeOTs in 2 mL of acetonitrile was kept at 70 °C for 6 h under argon. After cooling, the solution was added to a mixture of 1.20 g (6.00 mmol) of lauric acid and 0.506 g (5.00 mmol) of triethylamine in 2 mL of acetonitrile and heated at 70 °C for 48 h. The reaction mixture was treated with an ion-exchange resin (Amberlyst A-27). After evaporation and reprecipitation (chloroform–*n*-hexane), the polymeric materials were collected and dried in vacuo to give 0.62 g of **2** (73% yield).

Similarly, nonionic surfactant 4 of PNAI having a hydrophobic group at both ends was synthesized: ^{1}H NMR (entry 22, $CDCl_3$) δ 0.9 (t, CH_3CH_2), 1.2 (m, CCH_2C), 1.6 (m, $CH_2CH_2C(=O)O$), 2.1 (s, $CH_3C(=O)N$), 2.3 (t, $CCH_2C(=O)O$), 3.2–3.9 (br, CH_2N), 4.0 (m, $NCH_2CH=CH$), 4.2 (m, CCH_2O), 5.6 (m, CH=CH).

Measurements. ^{1}H NMR spectra were recorded on a 250-MHz Bruker AC250T spectrometer. Gel permeation chromatographic (GPC) analysis was performed by using a Tosoh SC-8010 with an RI detector under the following conditions: a Hitachi GL-A130 column with chloroform eluent at a flow rate of 1.0 mL/min. The surface tension (γ) of the aqueous solutions was measured by a Shimadzu Du Noüy tensiometer at ambient temperature, and the γ values obtained were recalculated to the value at 25 °C.[4,5]

References and Notes

(1) The term "electrophilic polymerization" for the cationic polymerization used here was proposed by: Kobayashi, S. Ring-Opening Polymerization. *ACS Symp. Ser.* **1985**, *No. 286*, 293.

(2) For recent papers on 2-oxazoline polymerizations, see: (a) Kobayashi, S.; Kaku, M.; Saegusa, T. *Macromolecules* **1988**, *21*, 1921. (b) Kim, J.; Litt, M. H. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2711. (c) Cai, G.; Litt, M. H. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 3603. (d) Chujo, Y.; Ihara, E.; Ihara, H.; Saegusa, T. *Macromolecules* **1989**, *22*, 2040. (e) Miyamoto, M.; Aoi, K.; Saegusa, T. *Macromolecules* **1989**, *22*, 3540. (f) Kobayashi, S.; Uyama, H.; Narita, Y. *Polym. J.* **1990**, *22*, 175. (g) Kobayashi, S. *Prog. Polym. Sci.* **1990**, *15*, 751.

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Registry No. **4** (R_1 = Me, R_2 = n-C_7H_{15}), 134757-18-9; **4** (R_1 = Me, R_2 = n-$C_{11}H_{23}$), 134757-19-0; **4** (R_1 = Me, R_2 = n-$C_{17}H_{35}$), 134757-20-3; **4** (R_1 = Me, R_2 = n-$C_8H_{17}CH=CH(CH_2)_7$), 134757-21-4; **4** (R_1 = Et, R_2 = n-$C_{11}H_{23}$), 134757-22-5; MeOZO, 1120-64-5; EtOZO, 10431-98-8; MeOTs, 80-48-8; $Me(N(Ac)(CH_2)_2)_nOCO(CH_2)_{11}H$, 134757-23-6; $Me(N(Ac)(CH_2)_2)_nOCO(CH_2)_7H$, 134757-24-7; $Me(N(Ac)(CH_2)_2)_nOCO(CH_2)_{17}H$, 134757-25-8; $Me(N(Ac)(CH_2)_2)_nOCO(CH_2)_{13}H$, 134781-01-4; $Me(N(Ac)(CH_2)_2)_nOCO(CH_2)_{15}H$, 134757-26-9; $Me(N(Ac)(CH_2)_2)_nOCO(CH_2)_7CH=CH(CH_2)_8H$, 134757-27-0; $Me(N(Ac)(CH_2)_2)_nOCO(CH_2)_7H$, 134757-28-1; $Me(N(COEt)(CH_2)_2)_nOCO(CH_2)_{11}H$, 134757-29-2; $Me(N(COEt)(CH_2)_2)_nOCO(CH_2)_{17}H$, 134757-30-5.