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Block Copolymerization of Vinyl Ether with Cyclic Imino Ether: Synthesis of a New Cleavable, Nonionic Polymer Surfactant

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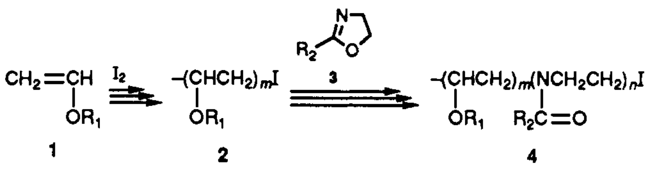
ABSTRACT: Block copolymers from vinyl ether and cyclic imino ether monomers were synthesized by successive cationic copolymerization of each monomer in a one-pot procedure. The resulting copolymers had a hydrophobic poly(vinyl ether) segment and a hydrophilic poly(*N*-acylalkylenimine) segment from the cyclic imino ether. Vinyl ethers used for construction of a hydrophobic segment are *n*-butyl, *i*-octyl, and *n*-cetyl vinyl ethers. Cyclic imino ethers used for construction of a 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 good surface activities and, hence, are a family of nonionic polymer surfactants. The surface activities reflected by the surface tension (γ) in water were high. The lowest γ value reached 27.6 dyn/cm for the copolymer from *n*-butyl vinyl ether/2-methyl-2-oxazoline. The C–N bond between the poly(vinyl ether) segment and poly(*N*-acylalkylenimine) segment was readily cleaved under acidic conditions to give a mixture of both homopolymers having no surface activities.

Introduction

Recently much attention has been paid to cleavable surfactants, which can be converted to nonsurfactant products under mild conditions. Surface activity of the cleavable surfactant can be readily altered when it becomes unnecessary. Some examples of synthesis and applications of monomeric cleavable surfactants have been reported.[1]

Cationic polymerization of cyclic imino ethers provides a convenient, versatile method for producing linear poly(*N*-acylalkylenimines).[2] Poly(*N*-acylalkylenimines) become hydrophilic or hydrophobic by changing the nature of the acyl group. By utilizing these characteristics, we have recently prepared new nonionic surfactants containing a hydrophilic poly(*N*-acylalkylenimine) segment.[3]

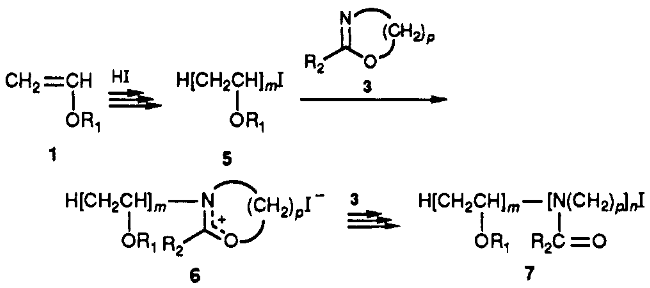
Syntheses of various block copolymers containing poly(*N*-acylalkylenimines) have been reported.[4] Very recently we have reported that block copolymers from poly(oxytetramethylene) and poly(*N*-acylalkylenimines) were synthesized in one pot by utilizing the living nature of the cationic ring-opening polymerization of the two monomers.[5] The block copolymer had a hydrophobic poly(oxytetramethylene) segment and a hydrophilic poly(*N*-acylalkylenimine) segment in the same molecule and, hence, showed good surface activities. Poly(vinyl ether)-*block*-poly(*N*-acylethylenimine) 4 was synthesized by ring-opening polymerization of a cyclic imino ether 3 in which the polymerization was supposed to be initiated by an iodomethyl group at the end of poly(vinyl ether) 2.[6] In addition to the above polymerization, the cationic polymerization of vinyl ethers was extended by using hydrogen iodide as an initiator.[7]



The present paper deals with one-pot synthesis, surface properties and hydrolytic lability of block copolymers consisting of a hydrophobic poly(vinyl ether) segment and a hydrophilic poly(*N*-acylalkylenimine) segment.

Results and Discussion

Synthesis of Block Copolymers. *n*-Butyl, *i*-octyl, and *n*-cetyl vinyl ethers were used to construct a hydrophobic segment. 2-Methyl- and 2-ethyl-2-oxazoline (MeOZO and EtOZO, respectively) and 2-methyl-5,6-dihydro-4*H*-1,3-oxazine (MeOZI) were used to provide a hydrophilic segment. The polymerization of vinyl ether 1 was performed with hydrogen iodide as an initiator in hexane at −20 °C for 4 h to produce the propagating species of poly(vinyl ether) 5. Then, a cyclic imino ether 3 was added to the polymerization mixture at −78 °C and allowed to react with 5 to produce poly(vinyl ether) 6 having oxazolinium groups at their termini. The polymerization of 3 was continued from 6 to give poly(vinyl ether)-*block*-poly(*N*-acylalkylenimine) 7.



For comparison, copolymer 4 has been prepared according to the literature method in which molecular iodine was used as initiator.[6] The polymerization of 2-oxazoline was induced by an iodomethyl group of 2, which was formed by the reaction of iodine with a vinyl ether at the initiation stage.

Figures 1 and 2 show ^{1}H and ^{13}C NMR spectra of block copolymers 4 and 7, respectively. The peak c in Figure 1B is due to the methyne proton of poly(vinyl ether) adjacent to poly(*N*-acylalkylenimine), and the corresponding peak is not detected in Figure 1A. In Figure 2B the peak of the methyne carbon is observed at 85.4 ppm;

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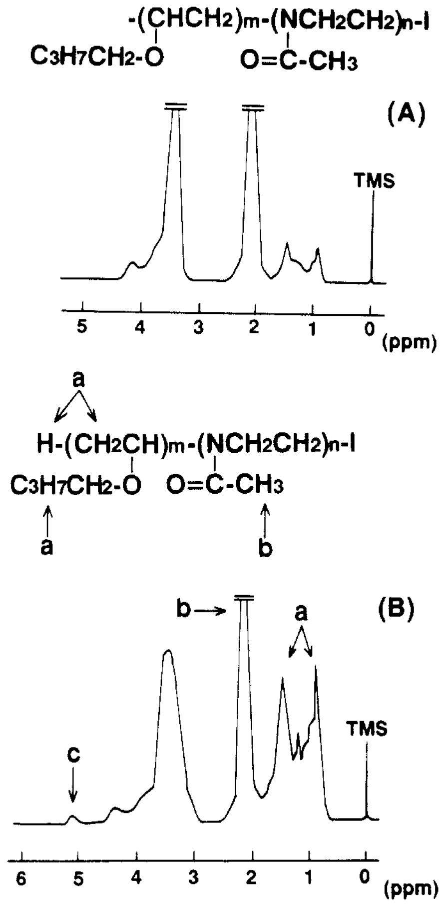


Figure 1. ^{1}H NMR spectra of 4 (A) and 7 (entry 2) (B).

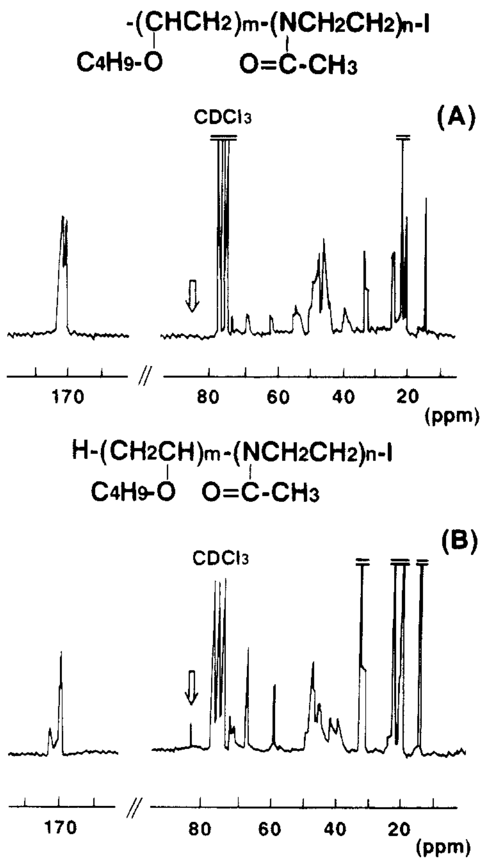


Figure 2. ^{13}C NMR spectra of 4 (A) and 7 (entry 2) (B).

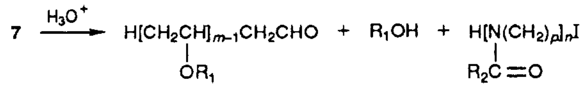
however, the corresponding peak is not detected in Figure 2A. These results clearly indicate that the structure of 7 is different from that of 4 as discussed above.

Copolymerization results are shown in Table I. The yield of copolymers was quantitative or very high. From ^{1}H NMR spectrum of 7, the unit ratio (m:n) was calculated by the integrated ratio of peaks a and b (Figure 1B). The composition was determined from the unit ratio and the molecular weight obtained by vapor pressure osmometry (VPO). It is seen that the chain length of copolymer is close to the charge ratio. This means that the propagating end 5 reacts with a cyclic imino ether quantitatively to give polymer 6, having the oxazolinium group at the terminal. Subsequent polymerization of the cyclic imino ether by 6 is very facile. The molecular weight distribution (M_w/M_n) obtained by gel permeation chromatography (GPC) was fairly narrow.

Surface Activities of Copolymer 7. The surfactant properties of polymer 7 were evaluated by measuring the surface tension (γ) in water. The γ values were obtained with aqueous polymer solutions of 0.5 wt %, which was higher than the critical micelle concentration (cmc) as shown in Figure 3. Surface activities reflected by the surface tension (γ) are dependent on the nature of R_1 and R_2 as well as the values of m and n. As a hydrophobic group (R_1), an ethyl group is not suitable; the copolymer (entry 1) is probably too hydrophilic. Polymers using n-butyl and i-octyl groups in R_1 (entries 2–8) showed good surfactant properties. Among them polymer sample 2 exhibited the lowest γ value of 27.6 dyn/cm. As a whole, the longer chain in R_1 of copolymer 7 does not increase the surfactant properties. For construction of a hydrophilic segment, three monomers examined were efficient; γ values of polymer samples 5, 7, and 8 were very low and almost the same.[3,5] The chain length of a hydrophilic segment $n \sim 5$ showed better surface activity than that of $n \sim 10$ (entries 2, 3, 5, and 6).

Cleavable Property of Copolymer 7. The tertiary carbon bonding the poly(vinyl ether) segment to the poly(N-acylalkylenimine) segment possesses an alkoxyl group and an amide group and, hence, is expected to be hydrolyzed easily under acidic conditions. The cleavage of copolymer 7 (entry 3) in an aqueous solution was examined under various conditions. The degree of cleavage of 7 was determined by ^{1}H NMR analysis of the product after hydrolysis. The copolymner was stable under neutral and basic conditions (Table II). However, the copolymer completely cleaved in 0.1 N HCl solution. In a less acidic solution (0.001 N HCl), the rate of cleavage was slower. The peak at 85.4 ppm in the ^{13}C NMR spectrum (Figure 2B) due to the tertiary carbon atom completely disappeared after 1 day in 0.1 N HCl solution. This can be taken to support the hypothesis that the hydrolysis proceeded quantitatively.

The hydrolysis of copolymer may proceed as follows.



$$7 \xrightarrow{H_3O^+} H[\underset{OR_1}{CH_2CH}]_{m-1}CH_2CHO + R_1OH + H[\underset{R_2C=O}{N}(CH_2)_p]_nI$$

After hydrolysis of 7, each homopolymer segment was separated by reprecipitation (methanol–diethyl ether). The diethyl ether soluble portion contained mainly poly(vinyl ether) fragments and showed a peak at 1720 cm^{-1} in the IR spectrum. This indicates that the terminal group of poly(vinyl ether) fragments possesses an aldehyde group. The diethyl ether insoluble portion contains mainly poly(N-acylalkylenimine) fragments, soluble in water. The γ value of its aqueous solution was 65.2 dyn/cm, which demonstrates that the surface activity of 7 disappeared

Table I
Block Copolymerization and Copolymers of Vinyl Ethers and Cyclic Imino Ethers

	block copolymerizn[a]					block copolymer 7					
entry no.	R_1	R_2	p	$\frac{[1]_0}{[HI]_0}$	$\frac{[3]_0}{[HI]_0}$	yield, %	M_n[b]	m[c]	n[c]	M_w/M_n[d]	γ,[e] dyn/cm
1	Et	Me	2	5.0	4.8	91	838	4.3	4.7	1.34	53.1
2	*n*-Bu	Me	2	3.1	5.3	90	927	3.0	5.9	1.44	27.6
3	*n*-Bu	Me	2	3.1	10.6	93	1300	2.7	10.5	1.35	32.7
4	*n*-Bu	Me	2	5.2	9.7	92	1350	4.5	9.0	1.32	33.6
5	*i*-Oc	Me	2	2.9	5.5	90	1010	2.8	5.3	1.26	28.7
6	*i*-Oc	Me	2	3.3	9.9	94	1500	3.1	10.5	1.22	31.5
7	*i*-Oc	Et	2	2.9	4.8	92	997	2.7	4.7	1.42	30.4
8	*i*-Oc	Me	3	2.9	4.6	95	1000	2.9	4.2	1.47	30.6
9	*n*-Cet	Me	2	1.1	5.7	97	979	1.3	5.8	1.42	38.4
10	*n*-Cet	Me	2	2.1	5.3	100	1020	1.8	4.7	1.28	34.6
11	*n*-Cet	Me	2	2.5	10.5	94	1660	2.6	9.9	1.34	45.1

[a] Polymerization of vinyl ether 1 at -20 °C for 4 h under nitrogen and then the polymerization of cyclic imino ether 3 at 80 °C for 8 h under nitrogen. [b] From VPO. [c] From VPO and ^{1}H NMR. [d] Obtained by GPC. [e] The surface tension (γ) 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.

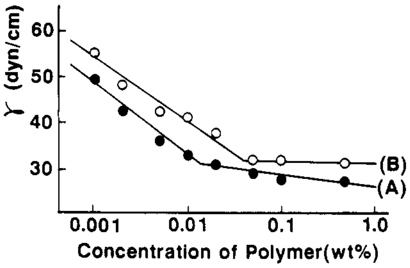


Figure 3. Polymer concentration–γ relationships: (A) polymer sample of entry 2; (B) polymer sample of entry 6.

Table II
Cleavage Reaction of 7 at 25 °C[a]

solvent	time, h	cleavage,[b] %
water	24	<5
0.001 N HCl	24	75
0.1 N HCl	1	>95
0.1 N HCl	2	100
0.1 N NaOH	24	<5

[a] [7] (entry 3) = 8.0×10^{-3} mol/L. [b] By ^{1}H NMR.

after hydrolysis. Copolymer 7 is the first example of a cleavable surfactant of a block copolymer.

Experimental Section

Materials. Solvents, *n*-hexane, chloroform, and acetonitrile were purified in the usual manner. MeOZO and EtOZO were purified by distillation over potassium hydroxide. *n*-Cetyl vinyl ether was supplied by Shin-nihon Rika Co. and purified by distillation. Other alkyl vinyl ethers were purified by distillation over calcium hydride. MeOZI was prepared according to the literature.[8] Iodine was purified by sublimation. Hydrogen iodide hexane solution was prepared according to the literature[7a] and titrated before use. All operations were carried out under nitrogen.

Synthesis of Block Copolymer 4.[6] Under nitrogen, 3.99 g (15.7 mmol) of iodine in 300 mL of *n*-hexane was cooled to 0 °C, and 3.1 g (31.0 mmol) of *n*-butyl vinyl ether in 5 mL of *n*-hexane was added to the mixture. Polymerization was performed at 0 °C for 2 h. Anhydrous sodium thiosulfate was added, and the mixture was stirred for 2 h. After filtration, the filtrate was dried over calcium hydride, followed by evaporation of the solvent to give 3.79 g (74% yield) of 2. The molecular weight of 2 was 390 by VPO. Then, 0.850 g (2.18 mmol) of 2 and 0.635 g (7.50 mmol) of MeOZO in 5 mL each of acetonitrile and chloroform were heated at 80 °C for 12 h under nitrogen. The reaction mixture was poured into a large amount of *n*-hexane to give 0.773 g (52% yield) of 4. The molecular weight of 4 was 2420, and the M_w/M_n value of 4 was 2.39. The composition (*n*-butyl vinyl ether: MeOZO) of 4 determined by ^{1}H NMR and VPO is 3.8:22.5. ^{1}H NMR of 2 ($CDCl_3$): δ 0.8–1.9 (m, CH_3 and CCH_2C), 3.1–3.9 (m, CCH_2O, CCHO, CH_2I). ^{1}H NMR of 4 ($CDCl_3$): δ 0.8–1.8 (m, CH_3C and CCH_2C), 2.0 (s, $CH_3C{=}O$), 3.0–4.2 (br, CCH_2C, CCHO, CCH_2N).

Synthesis of Block Copolymer 7. A typical run was as follows (entry 2). Under nitrogen, 0.43 g (4.29 mmol) of *n*-butyl vinyl ether in 5 mL of *n*-hexane was cooled to -78 °C, and 2 mL (1.4 mmol) of 0.7 N hydrogen iodide–*n*-hexane solution was added to the mixture. The reaction mixture was allowed to stand at -20 °C for 4 h. After the mixture was cooled to -78 °C, 0.633 g (7.44 mmol) of MeOZO was added. Then, 10 mL of acetonitrile was added to the mixture, and the mixture was heated at 80 °C for 8 h. The solvents were evaporated, and the remaining polymeric materials were dried in vacuo to give 1.17 g (90% yield) of 7. ^{1}H NMR ($CDCl_3$): δ 0.8–1.7 (m, CH_3C and CCH_2C), 2.0 (s, $CH_3C{=}O$), 3.0–4.4 (b, CCH_2O, CCHO, and CCH_2N), 5.0–5.2 (m, OCHN).

Hydrolysis of Block Copolymer 7. Block copolymer 7 (entry 6) (0.727 g) was dissolved in 120 mL of 0.1 N HCl aqueous solution and was allowed to stand at 30 °C for 24 h. After evaporation, the residue was dissolved in 3 mL of methanol and the mixture was poured into 80 mL of diethyl ether. The portion, insoluble in diethyl ether, was dried in vacuo to give 0.411 g of the polymeric materials. The remaining ether solution was evaporated in vacuo to 0.179 g of oily product. ^{1}H NMR of diethyl ether insoluble portion (CD_3OD): δ 2.0 (s, $CH_3C{=}O$), 3.1–4.2 (br, CCH_2N). ^{1}H NMR of diethyl ether soluble portion ($CDCl_3$): δ 0.8–1.7 (m, CH_3C, CCH_2C, and CCHC), 2.5–2.7 (m, $CCH_2C{=}O$), 3.1–3.7 (m, CCH_2O and CCHO). IR (neat): 1720 cm^{-1} ($\nu_{HC=O}$).

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 a Jasco Trirotor with RI and UV detectors under the following conditions: a Shodex K-802 or AC-803 column with chloroform eluent; flow rate, 1.0 or 0.5 mL/min. The molecular weight of polymers was measured by a Corona 117 vapor pressure osmometer (VPO) in chloroform at 40 °C. The surface tension (γ) of aqueous polymer solutions was measured by a Shimadzu Du Noüy tensiometer at ambient temperature, and the values obtained were recalculated to the values at 25 °C.

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