was dissolved in acetonitrile (2 ml) containing 0.04 mmol of *p*-methoxyphenol as a radical inhibitor under nitrogen. After the tube was maintained at 60 °C for 15 h, the reaction mixture was poured into a large amount of diethyl ether to precipitate the copolymer. After purification, the copolymer was dried in vacuo and weighed. The structure was determined by IR, NMR, and elemental analyses. The analytical data of the 1:1 copolymers are shown in Tables II and III.

In the cases of the copolymerization with BPL, the procedure was similar but the radical inhibitor was not added. The copolymer composition was determined by NMR. All the results are shown in Table I.

Molecular Weight Determination. The molecular weights of the cpolymers were measured by a vapor pressure osmometer (Hitachi Perkin-Elmer Model 115) in DMF at 55 °C.

Alkaline Hydrolysis of Copolymer. To 0.05 g of copolymer was added 1.0 ml of a 10% solution of NaOH in D_2O, and the reaction mixture was refluxed for 3 h. Then, the reaction mixture was subjected to NMR measurement. The NMR spectrum was compared with that of authentic compounds in alkaline D_2O solution. The results were as follows; the hydrolysis mixture of **1a**, i.e., **3** + HCO_2Na: NMR (D_2O) δ 8.40 (s, HCO_2Na, 1 H), 3.60 (t, OCH_2, 2 H), 2.64 (t, $-CH_2NCH_2-$, 4 H), 2.33 (t, CH_2CO_2, 2 H); the hydrolysis mixture of **2a**, i.e., **4** + HCO_2Na: NMR (D_2O) δ 8.40 (s, HCO_2Na, 1 H), 3.58 (t, OCH_2, 2 H), 2.16–2.95 (m, $CH_2NCH_2CH_2CO_2$, 6 H), 1.66 (m, CCH_2C, 2 H).

Isolation of Zwitterion 10 from PhOZI and AA. At 0 °C under nitrogen, 1.21 g (7.5 mmol) of PhOZI and 0.54 g (7.5 mmol) of AA were dissolved in 2 ml of acetonitrile in a tube. The tube was then sealed and maintained at 5 °C for 10 days. The solution was poured into an excess of diethyl ether to yield an oily product, which was dissolved in 3 ml of methylene chloride and reprecipitated in diethyl ether to give a white crystalline material. By filtration and drying 0.184 g of product **10** was isolated (11%), mp 145–146 °C. The structure was determined by the usual methods; NMR ($CDCl_3$) δ 2.28 (m, CCH_2C, 2 H), 2.50 (t, J_H = 7 Hz, CH_2CO_2, 2 H), 2.97 (t, J_H = 7 Hz, $-CH_2NCH_2-$, 4 H), 4.62 (t, J_H = 7 Hz, OCH_2, 2 H), 7.60 (m, C_6H_5C, 5 H); IR (KBr) 3430, 2960, 1725 (CO_2H), 1630 ($\nu_{C=N}$), 1400, 1280, 1110, 860, 710, etc., cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO_3(H_2O)$: C, 62.18; H, 6.82; N, 5.57. Found: C, 61.63; H, 6.76; N, 5.51. The water in the hydrate would have been incorporated during work-up.

The polymerization of **10** was carried out as follows, i.e., 0.3 g of **10** was heated to 150 °C to melt it and then maintained at 120 °C for 5 h under vacuum. The product was dissolved in 1 ml of chloroform and reprecipitated into an excess of diethyl ether. The yield of polymer **2c** was quantitative.

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Polymerization via Zwitterion. 15. Alternating Copolymerizations of Cyclic Imino Ethers with Hydroxyalkyl Acrylates Involving Hydrogen Transfer of the Acrylates

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ABSTRACT: This paper describes an extension of studies on the no catalyst copolymerization, in which a nucleophilic monomer (M_N) and an electrophilic monomer (M_E) are mixed to produce the key intermediate of a zwitterion. In the present study, M_N monomer is a cyclic imino ether, i.e., 5,6-dihydro-4*H*-1,3-oxazine (OZI) or 2-methyl-2-oxazoline (MeOZO), and M_E monomer is 2-hydroxyethyl (HEA) or 3-hydroxypropyl acrylate (HPA). Reactions of the 1:1 monomer feed ratio gave 1:1 alternating copolymers of **3a**, **3b**, **3c**, and **3d**, respectively, from the combinations of OZI–HEA, OZI–HPA, MeOZO–HEA, and MeOZO–HPA without any added catalyst. A mechanism via zwitterion intermediate **8** was proposed, which involves the proton-transfer step from the hydroxy group (OH) to generate a zwitterion **8**. The produced copolymer **3** is composed of three functional groups of amide, ester, and ether.

The present paper describes an extension of studies on the no catalyst copolymerization,[1] in which a nucleophilic monomer (M_N) and an electrophilic monomer (M_E) are mixed to produce the key intermediate of a zwitterion. Alternating copolymerization of 2-oxazoline (M_N) with acrylic acid (M_E) to produce a copolymer of amide–ester type structure **1** has recently been described.[2] The interconversion of acrylic acid (AA) to the ester unit in **1** involves a proton-transfer step of the acid (Scheme I).

In a similar way, cyclic imino ethers were copolymerized with acrylamide (AM) to produce 1:1 alternating copolymers having amide–imidate structure, e.g., **2**, which were also supposed to be copolymers produced via zwitterions.[3] These findings prompted us to examine the copolymerizations of hydroxyalkyl acrylate as M_E which is also capable of proton transfer. In the present study, a hydroxyalkyl acrylate, 2-hydroxyethyl acrylate (HEA) or 3-hydroxypropyl acrylate, was paired with M_N of cyclic imino ethers of 5,6-dihydro-4*H*-1,3-oxazine (OZI) and 2-methyl-2-oxazoline (MeOZO). In all of the four combinations of M_N and M_E, the alternating

Table I
1:1 Alternating Copolymerization of Cyclic Imino Ether (M_N) with Hydroxyalkyl Acrylate (M_E)

No.	M_N[a]	M_E[a]	Solvent (ml)	Temp, °C	Time, h	Copolymer yield, %	Copolymer structure (M_N/M_E)	Mol wt[b]
1	OZI	HEA	Acetonitrile (1.0)	60	30	78	**3a** (50/50)[c]	850
2	OZI	HEA	Acetonitrile (1.0)	80	20	82	**3a** (50/50)[c]	1040
3	OZI	HPA	DMF (1.0)	70	70	51	**3b** (50/50)[c]	1210
4	MeOZO	HEA	Acetonitrile (1.0)	80	50	65	**3c** (50/50)[d]	2390
5	MeOZO	HEA	DMF (0.5)	70	70	66	**3c** (50/50)[d]	
6	MeOZO	HPA	DMF (0.5)	70	70	42	**3d** (50/50)[d]	1530

[a] 5 mmol each. [b] Determined by vapor pressure osmometry. [c] Very hygroscopic. [d] Insoluble in water.

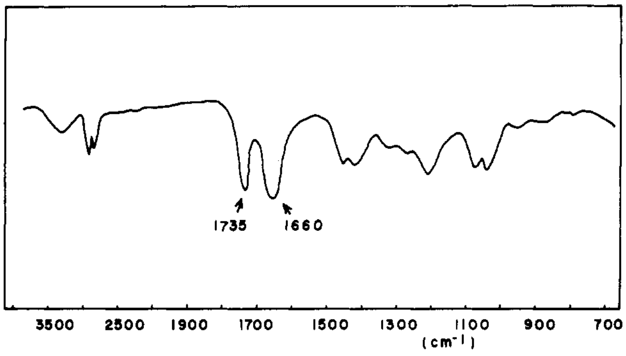


Figure 1. IR spectrum of the OZI–HEA copolymer **3a** (KBr).

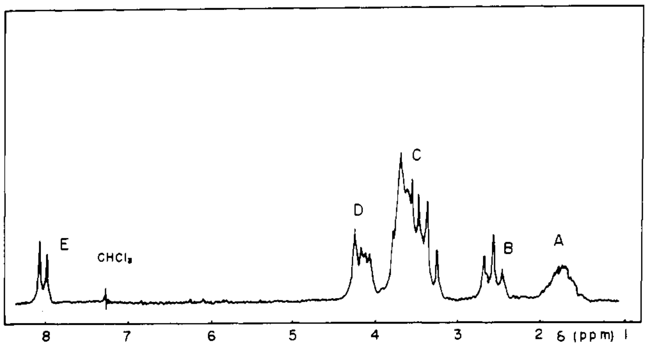
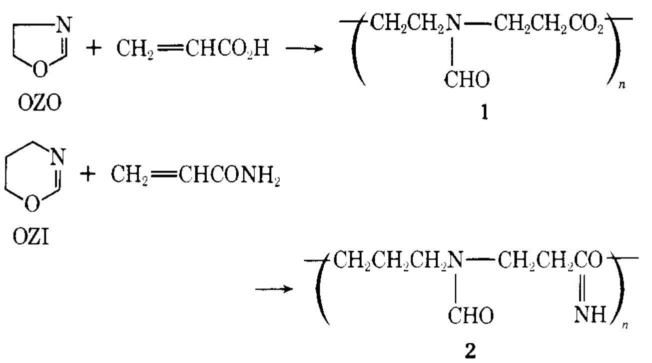
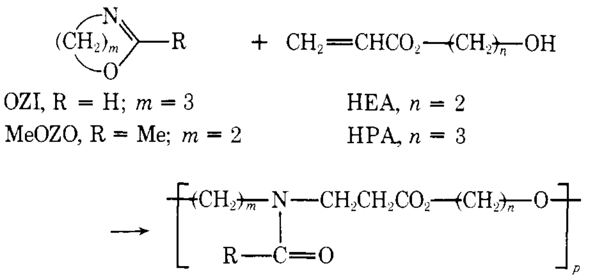


Figure 2. NMR spectrum of the OZI–HEA copolymer **3a** (in $CDCl_3$).

Scheme I



copolymers **3** were produced without any added catalyst (eq 1).



(1)

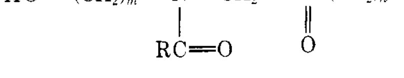
3a, R = H; $m = 3$; $n = 2$
b, R = H; $m = n = 3$
c, R = Me; $m = n = 2$
d, R = Me; $m = 2$; $n = 3$

Results and Discussion

Alternating Copolymerizations. OZI and HEA were allowed to react with each other at 80 °C in acetonitrile in a sealed tube under nitrogen. Polymerization took place without any added initiator, and the polymeric material was collected by a usual work-up. It was a pale yellow gum, which was soluble in polar solvents such as DMF, chloroform, methanol, and water, but insoluble in diethyl ether and benzene. The molecular weight was not high (see Table I).

The structure of the copolymer was determined by NMR and IR spectroscopy and elemental analysis as well as the identification of the alkaline hydrolysis products. Typical IR and NMR spectra are shown in Figures 1 and 2, respectively. The assignments of the peaks are described in Table III. It is evident from the NMR spectrum that the carbonyl methylene group (CH_2CO_2) (at δ 2.55) is present but olefinic bond is not.

The results of elemental analyses of four alternating copolymers (samples of No. 2 (**3a**), 3 (**3b**), 4 (**3c**), and 6 (**3d**)) are shown in Table II. With samples No. 2, 3, and 6, the observed values of carbon and nitrogen contents are lower than the respective calculated values. For these differences, two possibilities may be considered. One is due to the end groups, since the molecular weights of these copolymers are low (Table I). As the end groups, hydroxy group is assumed, which is derived by the reaction of growing species with water during work-up.



$$HO-(CH_2)_m-\underset{\substack{|\\ RC=O}}{N}-CH_2-\underset{\substack{\|\\ O}}{C}O(CH_2)_n-OH$$

The IR absorption at 3200–3400 cm^{-1} may be ascribed to the OH end groups. The values in parentheses of elemental analysis (in Table II) have been calculated on the basis of the above assumption of end groups. The other possibility for the difference of elemental analysis is the occluded water, since the copolymers are highly hygroscopic. At any rate, the formations of 1:1 alternating copolymers are shown by the experimental values of the atomic ratios of carbon to nitrogen which are in good agreement with the calculated ones.

A further support of the structure **3a** was obtained by its alkaline hydrolysis products. As described in the Experimental Section, the NMR spectrum of the hydrolysis mixture

Table II
Elemental Analyses of Copolymers

No.[a]	Formula[b]	Calcd[c] for 1:1 copolymer C	H	N	Found for 1:1 copolymer C	H	N	Ratio C/N
2	$C_9H_{15}NO_4$ $(C_9H_{15}NO_4(H_2O)_{0.2})$	53.73 (52.78)	7.46 (7.52)	6.96 (6.84)	52.10	7.43	6.52	9/0.96
3	$C_{10}H_{17}NO_4$ $(C_{10}H_{17}NO_4(H_2O)_{0.18})$	55.81 (55.67)	7.90 (8.05)	6.51 (6.49)	54.13	7.61	6.37	10/1.00
4	$C_9H_{15}NO_4$ $(C_9H_{15}NO_4(H_2O)_{0.084})$	53.72 (53.66)	7.51 (7.54)	6.96 (6.95)	53.90	7.21	6.95	9/0.99
6	$C_{10}H_{17}NO_4$ $(C_{10}H_{17}NO_4(H_2O)_{0.142})$	55.80 (55.70)	7.96 (8.02)	6.51 (6.49)	55.51	7.81	6.15	10/0.94

[a] Numbers of samples are the same as those of experiments in Table I. [b] Formulas in parentheses were given on the assumption of hydroxyl end groups. [c] Calculated values in parentheses are for the formulas in parentheses.

in D_2O showed the production of an equimolar mixture of **4** and **5**. It was shown by the comparison with the spectrum of a mixture of the two authentic samples (see Experimental Section).

$$\mathbf{3a} \xrightarrow{\text{NaOH}} \underset{\mathbf{4}}{HOCH_2CH_2OCH_2CH_2CH_2NHCH_2CH_2CO_2Na} + \underset{\mathbf{5}}{HCO_2Na} \quad (2)$$

Copolymerizations of the other three combinations of OZI-HPA, MeOZO-HEA, and MeOZO-HPA were carried out in a similar way, in which three alternating copolymers of **3b, 3c,** and **3d** were produced (Table I). The characterizations of the obtained copolymers are shown in Table III. The hydrolysis experiments were not undertaken in these three cases.

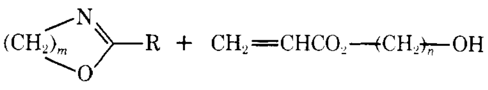
All copolymers, **3a–d,** are of amide–ester–ether type structure. Formation of the ester–ether unit from hydroxyalkyl acrylate (HAA) is interesting, in which a hydrogen transfer of the alcoholic proton of HAA is involved. In relation to this type of elementary process, a novel hydrogen-transfer polymerization of HAA is to be quoted here[4] (eq 3).

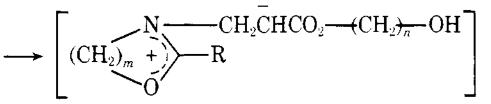
$$\underset{\substack{\text{HEA, } n = 2\\ \text{HPA, } n = 3}}{CH_2{=}CHCO_2(CH_2)_nOH} \xrightarrow{\text{base}} \underset{\substack{\mathbf{6a},\ n = 2\\ \mathbf{b},\ n = 3}}{-\!\!\left(CH_2CH_2CO_2(CH_2)_nO\right)_{\!p}\!\!-} \quad (3)$$

The present copolymerizations of HAA are the second example of the hydrogen-transfer polymerization of HAA. This polymerization is interestingly compared with the hydrogen-transfer polymerizations of acrylic acid[2,5] and of acrylamide.[3,6]

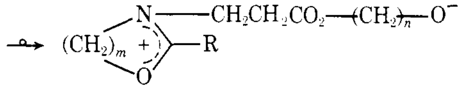
Although **3** was produced by an alternating copolymerization between a cyclic imino ether and a HAA, the structure of **3** can be taken as an alternating terpolymer, for example, **3a** can be regarded as a 1:1:1 alternating terpolymer from the OZI-β-propiolactone (BPL)–ethylene oxide (EO) system. Similarly, **3b, 3c,** and **3d** are alternating terpolymers of OZI–BPL–oxetane, MeOZO–BPL–EO, and MeOZO–BPL–oxetane, respectively. It is difficult to prepare such polymers by the terpolymerization of the three monomers. The present copolymerization, therefore, provides a new route to such polymers having three functional groups in the main chain.

Copolymerization Mechanism. A scheme via zwitterion intermediate **8** is proposed for the present copolymerization as in the cases of acrylic acid[2] and acrylamide.[3] In the course of the formation of **8**,





7



8

the addition adduct **7** is first formed. Then, an inter- and/or intramolecular proton transfer of the alcoholic proton to the carbanion **7** occurs to form the alkoxide anion **8**. The zwitterion **8** is a key intermediate in both the initiation and propagation reactions. These reactions proceed in the same manner as has been described in the no catalyst copolymerizations.[1] A lower molecular weight of copolymers may be ascribed to the lower stability of alkoxide anion of zwitterions in comparison with the case of acrylic acid.[2] The alkoxide anion is likely to cause side reactions such as hydrogen abstraction bringing about a chain transfer, while in the copolymerization of acrylic acid the stable carboxylate anion does not cause chain transfer.

Nonalternating Copolymerizations. The copolymerizations of HEA with 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (PhOZI) and unsubstituted 2-oxazoline (OZO) were also examined. Copolymerization occurred without any added catalyst, but both copolymers consisted of much more than 86 mol % of HEA units. HEA was found to be incorporated via hydrogen transfer to form the ester–ether unit. The biased

Table III
Spectroscopic Data of Copolymers

3a (pale yellow gum)
NMR ($CDCl_3$) δ 1.70 (m, CCH_2C, 2H), 2.55 (m, CH_2CO_2, 2 H), 3.60 (m, $-CH_2NCH_2-$ and $-CH_2OCH_2-$, 8 H), 4.15 (m, CO_2CH_2, 2 H), 8.01 (d, NCHO, 1 H)
IR (film) 1735 (ester), 1660 (amide), 1060 ($\nu_{C\text{-}O}$), etc., cm^{-1}
3b (yellow gum)
NMR ($CDCl_3$) δ 1.80 (m, two CCH_2C, 4 H), 2.51 (m, CH_2CO_2, 2 H), 3.55 (m, $-CH_2NCH_2-$ and $-CH_2OCH_2-$, 8 H), 4.13 (m, CO_2CH_2, 2 H), 8.02 (d, NCHO, 1 H)
IR (film) 1730 (ester), 1660 (amide), 1050 ($\nu_{C\text{-}O}$), etc., cm^{-1}
3c (colorless gum)
NMR ($CDCl_3$) δ 1.93 (broad singlet, $CH_3C{=}O$, 3 H), 2.34 (m, CH_2CO_2, 2 H), 3.70 (m, $-CH_2NCH_2-$ and $-CH_2OCH_2-$, 8 H), 4.18 (m, CO_2CH_2, 2 H)
IR (film) 1733 (ester), 1634 (amide), 1080 ($\nu_{C\text{-}O}$), etc., cm^{-1}
3d (colorless gum)
NMR ($CDCl_3$) δ 1.78 (m, CCH_2C, 2 H), 1.93 (broad singlet, $CH_3C{=}O$, 3 H), 2.35 (m, CH_2CO_2, 2 H), 3.60 (m, $-CH_2NCH_2-$ and $-CH_2OCH_2-$, 8 H), 4.12 (m, CO_2CH_2, 2 H)
IR (film) 1730 (ester), 1630 (amide), 1050 ($\nu_{C\text{-}O}$), etc., cm^{-1}

compositions of the copolymers may be ascribed to the decreased nucleophilic reactivities of PhOZI and OZO. The concentration of the key intermediate of zwitterion is low because the rate of generation is slow. Consequently, the homopolymerization of HEA involving hydrogen transfer[4] occurred in addition to the alternating propagation of the genetic zwitterion. These findings indicate that the combination between M_N and M_E monomer is a very important factor for alternating copolymerization.

Conclusive Remark. From the results of the present study together with those of the copolymerizations of acrylic acid[2] and acrylamide,[3] it should generally be said that electron deficient vinyl monomers having an acidic hydrogen are effective M_E monomers which are successfully combined with M_N monomers such as cyclic imino ethers to cause no catalyst copolymerization involving the proton transfer.

Experimental Section

Materials. Solvents of acetonitrile and DMF were purified as previously described.[2,3] Monomers, MeOZO, HEA, and HPA, were commercial reagents and purified by distillation under nitrogen before use. OZO,[7] OZI,[8] and PhOZI[9] were prepared and purified according to the method reported before.

The authentic sample, 10-hydroxy-4-aza-8-oxadecanoic acid sodium salt **4**, was prepared according to the following procedures. In step A, the ordinary Michael addition of ethylene glycol (0.30 mol) to acrylonitrile (0.15 mol) was carried out at 80 °C.

$$\mathrm{HOCH_2CH_2OH} \xrightarrow[\text{(A)}]{+\mathrm{CH_2{=}CHCN}} \underset{\mathbf{9}}{\mathrm{HOCH_2CH_2OCH_2CH_2CN}}$$

$$\xrightarrow[\text{(B)}]{\mathrm{LiAlH_4}} \underset{\mathbf{10}}{\mathrm{HOCH_2CH_2OCH_2CH_2CH_2NH_2}} \xrightarrow[\text{(C)}]{+\mathrm{BPL}} \xrightarrow{+\mathrm{NaOH}} \mathbf{4}$$

After 10 h the mixture was subjected to distillation to give **9** in a 75% yield based on acrylonitrile (bp 96 °C (0.4 Hg); lit.[10] 111–120 °C (1.5–3.0 mm)). In step B, **9** (0.1 mol) was reduced to **10** by use of $LiAlH_4$ (0.1 mol) in THF solvent in a usual manner (5% yield, bp 65 °C (0.2 mm); lit.[11] 131 °C (24 mm)). In step C, 10-hydroxy-4-aza-8-oxadecanoic acid was prepared by the equimolar (2.6 mmol each) reaction of **10** with β-propiolactone (BPL) in acetonitrile (2 ml) according to the reported procedures.[3,12] After removal of the solvent, an equimolar amount of aqueous NaOH was added to the reaction product. The sodium salt **4** thus isolated was recrystallized from a mixed solvent of ethanol and diethyl ether (86% yield). **4:** mp 268 °C; NMR (D_2O) δ 1.21 (m, CCH_2CC, 2 H), 2.55 (t, CH_2CO_2, 2 H), 3.25 (m, $-CH_2NCH_2-$, 4 H), 3.97 (m, $HOCH_2CH_2OCH_2$, 6 H); IR (KBr) 3400 cm^{-1} ($\nu_{O\text{-}H}$ and $\nu_{N\text{-}H}$) 1565 and 1405 cm^{-1} (CO_2^-), 1070 cm^{-1} ($\nu_{C\text{-}O}$), etc. Anal. Calcd for $C_8H_{16}NNaO_4(H_2O)_{3.0}$: C, 35.96; H, 6.04; N, 5.24. Found: C, 36.50; H, 5.92; N, 4.93.

Molecular Weight Determination. The molecular weight of the copolymer was measured by vapor pressure osmometry as described before.[2,3]

Copolymerizations of Cyclic Imino Ethers with HEA. A typical procedure was as follows. In a sealed tube, OZI and HEA (each 5 mmol) were mixed in 1.0 ml of acetonitrile. The mixture was then allowed to react under nitrogen at 80 °C. After 20 h, the mixture was poured into a large amount of diethyl ether to precipitate the polymeric material. The product was isolated by decantation and purified further by the reprecipitation from chloroform (solvent) to diethyl ether (nonsolvent). The obtained copolymer was dried in vacuo. These results are shown in Table I.

Table IV
Copolymerization of HEA with PhOZI and with OZO

M_N[a]	M_E[a]	Solvent[b]	Temp, °C	Time, h	Copolymer yield, %	Copolymer composition[c] M_N/M_E
PhOZI	HEA	Acetonitrile	100	100	8	14/86
OZO	HEA	Acetonitrile	80	40	20	10/90

[a] 5 mmol each. [b] 1.0 ml. [c] Determined by NMR spectroscopy.

The copolymerizations of PhOZI and OZO with HEA were carried out in a similar manner. However, the obtained copolymers were not of 1:1 composition. From the NMR spectroscopic study of them, the unit ratios between M_N and M_E were calculated. The results are shown in Table IV.

Alkaline Hydrolysis of Copolymer 3a. To 0.05 g of copolymer **3a** was added 0.5 ml of a 10% D_2O solution of NaOH at room temperature and the mixture was heated at 95 °C for 3 h. Then, the reaction mixture was directly subjected to NMR measurement: NMR δ 1.20 (m, 2 H), 2.55 (m, 2 H), 3.25 (m, 4 H), 3.96 (m, 6 H), 8.51 (s, 1 H). The spectrum was identical with that of 1:1 mixture of the authentic sample **4** and sodium formate **5**.

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