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Spontaneous 2:1 Sequence-Regulated Copolymerization of Cyclic Imino Ethers with Cyclic Carboxylic Anhydrides

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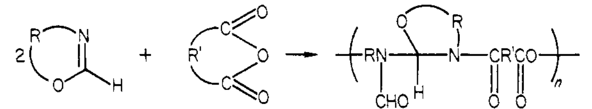
ABSTRACT: The present paper reports copolymerizations of two cyclic imino ethers, 2-oxazoline (OZO) and 5,6-dihydro-4*H*-1,3-oxazine (OZI), with two cyclic carboxylic anhydrides, succinic anhydride (SAn) and glutaric anhydride (GAn). The copolymerizations took place spontaneously around room temperature to 100 °C to produce 2:1 sequence-regulated copolymers (**1**). This result was explained by the concept of "no catalyst alternating copolymerization via zwitterion intermediate". Thus, OZO and OZI behaved as nucelophilic monomers (M_N) whereas SAn and GAn acted as electrophilic monomers (M_E). First, a 1:1 bicyclic adduct (such as **3**, **6**, and **7**) is formed by the reaction between M_N and M_E. Then the cyclic adduct behaved as M_E to react with another molecule of M_N, giving rise to a zwitterion like **5**, a key intermediate for the copolymerization, which has a 2:1 M_N/M_E composition. Subsequent reactions of these key intermediates led to the production of 2:1 sequence-regulated copolymers **1**.

In a series of studies on spontaneous copolymerization, cyclic imino ethers have served as reactive nucleophilic monomers (M_N) toward several electrophilic ones (M_E) such as β-propiolactone, acrylic acid, acrylamide, ethylenesulfonamide, and 3-hydroxy-1-propanesulfonic acid sultone.[1] This combination of M_N and M_E induced copolymerizations without added initiator to give in most cases 1:1 alternating copolymers via zwitterion intermediates. The present paper deals with spontaneous copolymerizations of two cyclic imino ethers (M_N), 2-oxazoline (OZO) and 5,6-dihydro-4*H*-1,3-oxazine (OZI), with two cyclic carboxylic anhydrides (M_E), succinic anhydride (SAn) and glutaric anhydride (GAn). These copolymerizations produced 2:1 sequence-regulated copolymers (**1**) in which one OZO or OZI unit is incorporated in a ring-opened form and the other unit is formed via reaction of the carbon–nitrogen double bond of OZO or OZI.



(1)

OZO, R = $-(CH_2)_2-$
OZI, R = $-(CH_2)_3-$

SAn, R′ = $-(CH_2)_2-$
GAn, R′ = $-(CH_2)_3-$

1a, R = R′ = $-(CH_2)_2-$
b, R = $-(CH_2)_2-$; R′ = $-(CH_2)_3-$
c, R = R′ = $-(CH_2)_3-$

Results and Discussion

Copolymerization of 2-Oxazoline (OZO) with Succinic Anhydride (SAn). The copolymerization of OZO with SAn took place around room temperature without added intiator to give a hygroscopic powdery material which was soluble in organic solvents such as chloroform, DMF, and acetonitrile and in water. The initial feed molar ratio of OZO/SAn was varied from 0.33 to 4.0. The copolymer structure, however, did not change and the OZO/SAn composition of the copolymers was 2:1 in all cases (no. 1–6 in Table I).

The copolymer structure was determined by ^1H NMR spectroscopy with the product copolymer itself and with the alkaline hydrolysis products of the copolymer, by IR spectroscopy, and by elemental analysis. Figure 1 (top) shows the ^1H NMR spectrum of the copolymer (sample no. 3) in D_2O. A large signal centered at δ 2.54 is assigned to $C(O)CH_2CH_2C(O)$ (4 H), signals in the region δ 3.1–4.4 are due to methylene protons of OCH_2 and NCH_2 (8 H), and sharp peaks at δ 6.26 and 8.25 are ascribed, respectively, to the characteristic methine proton of NCHN (1 H) and to the formyl proton of NCHO (1 H). The IR spectrum of the copolymer showed bands at 1735 and 1665 cm^{-1} due to $\nu_{C=O}$ of ester and of amide, respectively. These results strongly suggest structure **1a** for the copolymer.

The middle spectrum of Figure 1 is the ^1H NMR spectrum of the alkaline hydrolysis mixture of the copolymer in NaOH–D_2O. This spectrum was essentially the same as that of a mixture of authentic samples of ethanolamine, succinic acid, and formic acid in a ratio of 2:1:2 in NaOH–D_2O and indicates the production of these compounds in the same molar ratio. The hydrolysis experiment was further performed in D_2O without NaOH at 80 °C for 11 h. The ^1H NMR spectrum of the reaction system is shown in the bottom spectrum of Figure 1. Under these reaction conditions the cleavage took place selectively at the methine carbon moiety of the five-membered ring to produce a 1:1 mixture of formic acid and the amide–ester type product of succinic acid **2**. The signal assignments

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Table I
Copolymerizations of Cyclic Imino Ethers (M_N) with Cyclic Carboxylic Anhydrides (M_E) under Various Reaction Conditions

	reaction conditions				copolymer				
							composition M_N unit, %		
no.	M_N/M_E feed[a]	solvent	temp, °C	time, h	yield,[b] %	MW[c]	NMR	hydrolysis[d]	structure
				OZO-SAn System					
1	0.33	CH_3CN	35	30	75		66	66	1a
2	1.0	DMF	35	30	71	800	67	67	1a
3	1.0	CH_3CN	~30	336	78	2320	69	67	1a
4	2.0	CD_3CN	35	120	64	1160	67	67	1a
5	2.0	CD_3CN	80	48	60	1920	67	66	1a
6	4.0	CH_3CN	35	120	83		68	67	1a
				OZO-GAn System					
7	1.0	CD_3CN	100	50	99	4970	67	65	1b
8	2.0	DMF	80	48	90	2100	67	66	1b
9	*e*	CH_3CN	80	56	99	3110	67		1b
				OZI-GAn System					
10	1.0	CH_3CN	80	48	73	1050	62	63	1c
11	2.0	CH_3CN	80	48	72	1580	64	64	1c
12	4.0	CH_3CN	80	64	66	2100	67	66	1c

[a] $[M_N]_0 + [M_E]_0 = 6.0$ mmol in 1.2 mL of solvent. [b] Theoretical yield is based on the 2:1 (M_N/M_E) composition of the copolymers. [c] Determined by vapor pressure osmometry in DMF at 55 °C for no. 2-5 and 7-9 and in $CHCl_3$ at 35 °C for no. 10-12. [d] From the relative ratio of a peak due to formic acid and signals due to succinic or glutaric acid in the ^1H NMR spectrum of the alkaline hydrolysis mixture. [e] 3.1 mmol of **3** in 1.2 mL of CH_3CN.

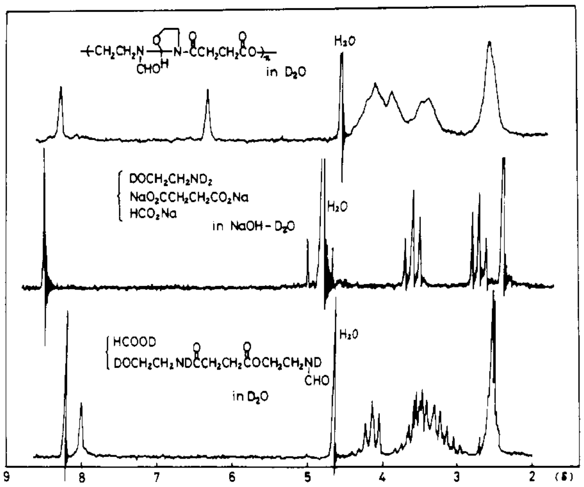
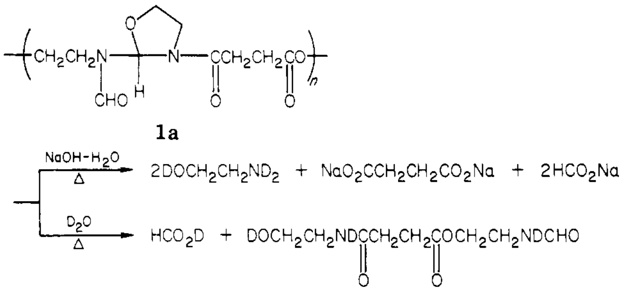


Figure 1. ^1H NMR spectra of copolymer **1a** in D_2O (top), of the alkaline hydrolysis mixture of **1a** in NaOH–D_2O (middle), and of the hydrolysis mixture of **1a** in D_2O (bottom).

are as follows: a signal at δ 2.60 due to $C(O)CH_2CH_2C(O)$ (4 H), a multiplet signal at δ 2.9–3.9, assigned to methylene protons of NCH_2 and of CH_2OH, a triplet-like signal at δ 4.15 due to $C(O)OCH_2$, and two sharp singlets at δ 8.00 and 8.20 due to >NCHO and HCO_2, respectively.



1a

2

All these data are well explained with the copolymer structure of **1a**. The copolymer composition was obtained by the signal integral ratio of the ^1H NMR spectra of the copolymer itself and of the alkaline hydrolysis mixture of the copolymer (Table I). Furthermore, the 2:1 copolymer composition was supported by elemental analysis (Table II). From the C/N atomic ratio the composition was calculated and the values are very close to those obtained by ^1H NMR spectroscopy, i.e., the unit molar ratio of OZO:SAn = 2:1.

Table II
Elemental Analyses of Copolymers

	found, %			composition M_N unit,[d] %
no.	C	H	N	
2[a]	47.62	5.89	10.72	64.7
3[a]	48.24	6.00	10.91	65.0
4[a]	47.55	6.43	10.71	64.8
6[a]	45.69	6.25	10.63	66.5
7[b]	50.41	6.37	10.04	63.7
8[b]	49.63	6.43	10.13	64.8
11[c]	53.76	7.31	9.67	66.8
12[c]	54.35	7.62	9.50	65.2

[a] Calcd for $(C_{10}H_{14}N_2O_5)_n$: C, 49.58; H, 5.83; N, 11.56. Calcd for $[C_{10}H_{14}N_2O_5(H_2O)_{1.00}]_n$: C, 45.96; H, 6.20; N, 10.76. [b] Calcd for $(C_{11}H_{16}N_2O_5)_n$: C, 51.56; H, 6.29; N, 10.93. Calcd for $[C_{11}H_{16}N_2O_5(H_2O)_{0.65}]_n$: C, 49.30; H, 6.50; N, 10.45. [c] Calcd for $(C_{13}H_{20}N_2O_5)_n$: C, 54.92; H, 7.09; N, 9.85. Calcd for $[C_{13}H_{20}N_2O_5(H_2O)_{0.30}]_n$: C, 53.89; H, 7.17; N, 9.67. [d] Obtained from the C/N ratio.

Copolymerization of 2-Oxazoline (OZO) with Glutaric Anhydride (GAn). At elevated temperatures, e.g., 100 °C, the copolymerization of OZO with GAn (1:1 feed) took place in acetonitrile to produce a pale yellow powdery material in quantitative yield (MW = 4970, no. 7 in Table I). The copolymer structure was examined in manner similar to that for the OZO-SAn system and was shown to be **2b**, the OZO/GAn ratio of the copolymer being 2:1. The top spectrum in Figure 2 is the ^1H NMR spectrum of the copolymer in $CDCl_3$. A signal at δ 1.6–2.2 is due to $CH_2CH_2CH_2$ (2 H), a peak at δ 2.2–2.7 is assigned to $C(O)CH_2CH_2CH_2C(O)$ (4 H), signals at δ 3.1–4.5 are due to methylene protons of NCH_2 and OCH_2 (total 8 H), and sharp singlets at δ 6.23 and 8.24 are ascribed, respectively,

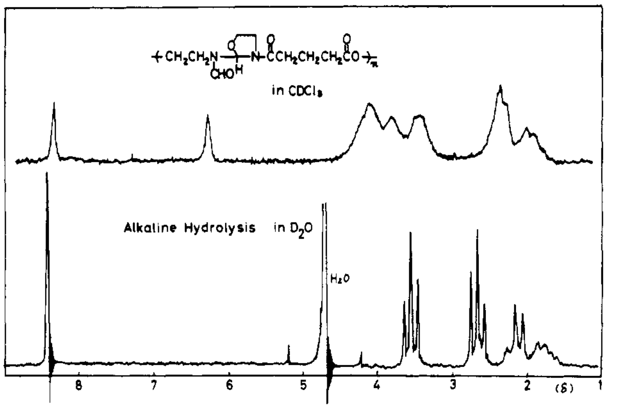
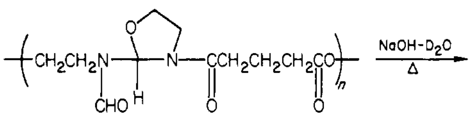


Figure 2. ^1H NMR spectra of copolymer **1b** in $CDCl_3$ (top) and of the alkaline hydrolysis mixture of **1b** in $NaOH-D_2O$ (bottom).

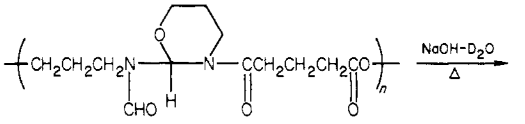
to the methine (1 H) and formyl (1 H) protons. The bottom spectrum of Figure 2 is the ^1H NMR spectrum of the alkaline hydrolysis mixture of the copolymer, indicating the formation of ethanolamine (triplet signals at δ 2.70 and 3.62), glutaric acid (signals at δ 1.6–2.0 and at 2.0–2.4), and formic acid (a sharp singlet at δ 8.40) in a ratio of 2:1:2. The IR spectrum of the copolymer shows carbonyl bands of ester (1735 cm^{-1}) and amide (1670 cm^{-1}), which support structure **1b**. Elemental analysis data are also compatible with the 2:1 copolymer composition (Table II).



1b

$2DOCH_2CH_2ND_2 + NaO_2CCH_2CH_2CH_2CO_2Na + 2HCO_2Na$

Copolymerization of 5,6-Dihydro-4*H*-1,3-oxazine (OZI) with Glutaric Anhydride (GAn). The copolymerization of OZI with GAn occurred at 80 °C in acetonitrile to produce a brownish, hygroscopic powdery material. The composition of the copolymer was always 2:1 (OZI/GAn) regardless of the initial feed molar ratio, e.g., OZI/GAn = 1.0, 2.0, and 4.0 (no. 10–12 in Table I). The ^1H NMR spectrum of the copolymer sample no. 11 in $CDCl_3$ (top spectrum of Figure 3) shows a signal at δ 1.5–2.1 due to $CH_2CH_2CH_2$ (total 6 H), a signal at δ 2.1–2.6, ascribed to $C(O)CH_2CH_2CH_2C(O)$ (4 H), signals at δ 3.0–4.3, attributed to OCH_2 and NCH_2 (total 8 H), a singlet at δ 6.25 due to the methine proton, and peaks at δ 7.98 and 8.16, ascribed to a proton of NCHO. The bottom spectrum of Figure 3 is the spectrum of the alkaline hydrolysis mixture of the copolymer. A multiplet at δ 1.4–2.0 is due to protons of $CH_2CH_2CH_2$ (6 H), a triplet-like signal centered at δ 2.10 is assigned to $C(O)CH_2$ (4 H), triplets at δ 2.60 and 3.55 are ascribed to OCH_2 and NCH_2, respectively, (4 H each), and a sharp singlet at δ 8.37 is due to HCO_2 (2 H). The results indicate that the alkaline hydrolysis of the copolymer produced 1,3-propanolamine, glutaric acid, and formic acid in a ratio of 2:1:2. The mixture of these three authentic compounds in the same ratio in $NaOH-H_2O$ showed a spectrum similar to that of the alkaline hydrolysis mixture of the copolymer carried out in $NaOH-H_2O$.



1c

$2DOCH_2CH_2CH_2ND_2 + NaO_2CCH_2CH_2CH_2CO_2Na + 2HCO_2Na$

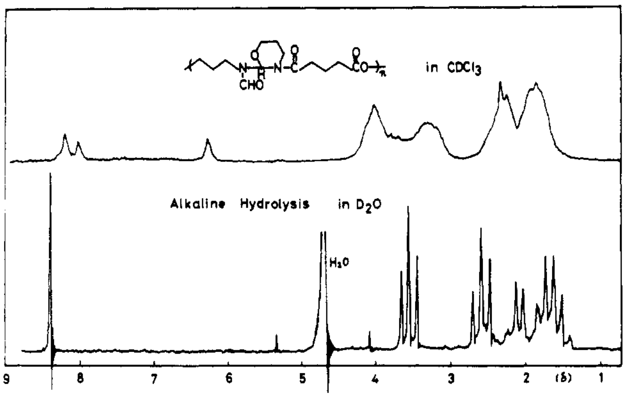


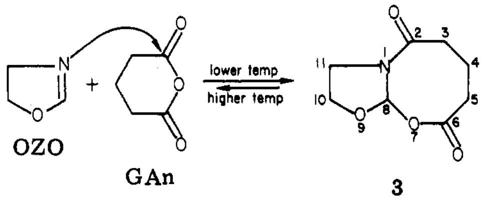
Figure 3. ^1H NMR spectra of copolymer **1c** in $CDCl_3$ (top) and of the alkaline hydrolysis mixture of **1c** in $NaOH-D_2O$ (bottom).

The IR spectrum of the copolymer showed carbonyl absorptions at 1740 cm^{-1} (ester) and 1660 cm^{-1} (amide). Elemental analyses supported the 2:1 composition of OZI and GAn (no. 11 and 12 in Table II).

All the above data strongly indicate the copolymer structure as **1c**. At present, however, the presence of two peaks around δ 8 (top spectrum, Figure 3) is not yet fully understood. Perhaps the presence of the *N*-formyl proton in cis and trans positions relative to the unsymmetrical alkyl groups causes the splitting of the signal.[2] Elucidation of this point requires further studies.

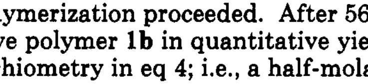
Copolymerization Mechanism. In all copolymerizations of the present study, the copolymer composition is 2:1 (M_N unit:M_E unit) regardless of the feed monomer ratio. A monomer of M_N or M_E in the feed in excess of the 2:1 stoichiometry remained unreacted after the copolymerization had been completed. In order to shed light on this phenomenon the copolymerization system was examined from the viewpoint of the reaction intermediate.

The reaction of OZO with GAn in acetonitrile took place at 0 °C and after 10 min gave quantitatively a very hygroscopic white solid, whose structure was determined as a 1:1 adduct of **3**. The structural determination of the



OZO GAn **3** (2)

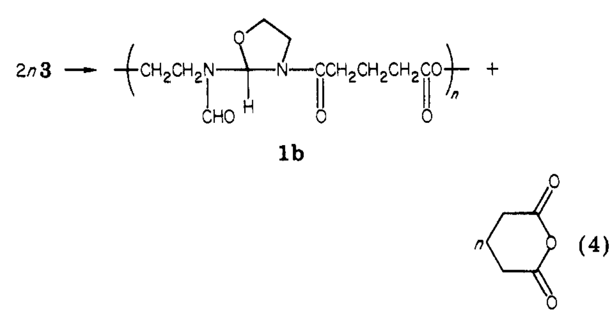
solid was made based on the following data: IR 1735 ($\nu_{C=O}$, ester), 1670 ($\nu_{C=O}$, amide), 1090 cm^{-1} (ν_{C-O}, ether); mp 87–88 °C. Anal. Calcd for $C_8H_{11}NO_4$: C, 51.89; H, 5.99; N, 7.56. Found: C, 51.66; H, 6.01; N, 7.75. The solid is insoluble in organic solvents and hence NMR measurement has not been achieved. The hydrolysis of the solid yielded a formic acid ester **4**. These data are compatible with the structure of the solid as 7,9-dioxa-1-azabicyclo[6.3.0]undecane-2,6-dione (**3**).[3]



$$3 \xrightarrow{H_2O} HCO_2CH_2CH_2NH\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2CO_2H \qquad (3)$$

4

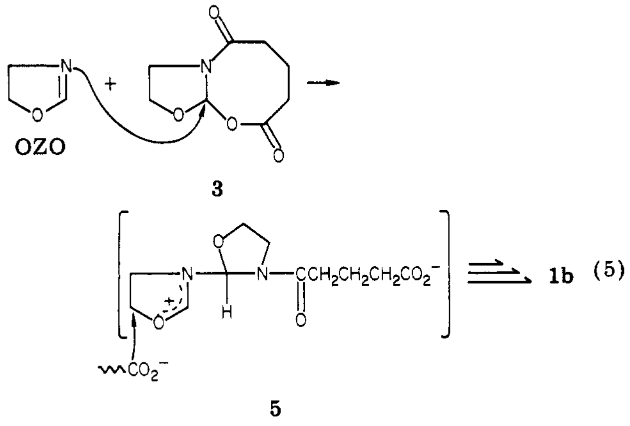
Then **3** was isolated and used as a starting monomer (no. 9 in Table I). In acetonitrile at 80 °C **3** gradually dissolved and the polymerization proceeded. After 56 h, the usual workup gave polymer **1b** in quantitative yield according to the stoichiometry in eq 4; i.e., a half-molar amount of GAn for **3** was recovered. This behavior indicates that **3** dissociates to OZO and GAn at higher temperatures and



1b

(4)

that the reaction of **3** with OZO gives the 2:1 unit given by **1b** as shown by reaction 5. The reaction of OZO with **3** involves nucleophilic attack of OZO at the methine carbon atom (C-8) of **3** to produce a 2:1 zwitterion **5**, which is a key intermediate for the copolymerization reaction 1. Subsequent reactions of **5** lead to the production of **1b**.[1] In the reaction (eq 5), OZO acted as M_N whereas **3** behaved as M_E. The attacking site of OZO at **3** is the methine carbon atom. The hydrolysis reaction (eq 3) proceeded in a similar manner; i.e., water attacked the methine carbon of **3** to produce **4**.



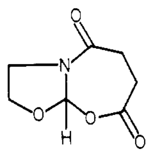
OZO

3

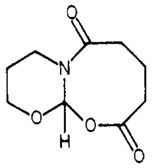
5

(5)

Reactions of OZO with SAn and of OZI with GAn produced bicyclic 1:1 adducts **6** and **7**, respectively. Isolation of **6**, however, has not been successful so far. Adduct **7** was quantitatively obtained by the reaction of OZI with GAn at lower temperatures. It is reasonable, therefore, that in these two combinations of copolymerization **6** and **7** are important intermediates and that they behaved as M_E which are formed in situ and then reacted with OZO and OZI as M_N to produce 2:1 sequence-regulated copolymers **1b** and **1c**, respectively.



6



7

Experimental Section

Materials. CH_3CN, CD_3CN, and DMF solvents were purified by distillation under nitrogen. Succinic anhydride (SAn) and glutaric anhydride (GAn) were purified by recrystallization from chloroform and from a chloroform–diethyl ether mixed solvent, respectively. 2-Oxazoline (OZO) and 5,6-dihydro-4*H*-1,3-oxazine (OZI) were prepared by reported procedures.[4,5]

Copolymerization. A typical run was as follows. In a glass tube, a mixture of OZO and SAn (3.0 mmol of each) was dissolved in 1.2 mL of CH_3CN under nitrogen. The tube was sealed and kept at 30 °C for 336 h. The copolymerization system was homogenous during the entire reaction. The reaction mixture was poured into 50 mL of diethyl ether to precipitate a polymeric material. This reprecipitation procedure was repeated two more times. The polymeric material was collected and dried in vacuo to give 0.28 g of a pale yellowish powdery material (78% yield, based on the 2:1 copolymer composition; i.e., OZO = 3.0 mmol and SAn = 1.5 mmol). The copolymer was very hygroscopic (MW = 2320).

Alkaline Hydrolysis of Copolymer. In 0.5 mL of 10% NaOH–D_2O solution was dissolved 0.03 g of copolymer (sample no. 3). The mixture was heated at 100 °C for 3 h. The ^1H NMR spectrum of the mixture is the middle spectrum of Figure 1, indicating that ethanolamine, succinic acid, and formic acid were produced in a ratio of 2:1:2. Since H–D exchange took place slightly at the methylene protons of $C(O)CH_2$ during the alkaline hydrolysis in D_2O, the hydrolysis was carried out in H_2O. The ^1H NMR spectrum of this reaction mixture was similar to that of a 2:1:2 mixture of ethanolamine, succinic acid, and formic acid in 10% NaOH–H_2O solution.

Hydrolysis of Copolymer. A copolymer (sample no. 3, 0.125 g) was dissolved in D_2O and kept at 80 °C for 8 h. The ^1H NMR spectrum of the reaction mixture is the bottom spectrum of Figure 1. A similar hydrolysis experiment was carried out in H_2O. In addition to water, formic acid was trapped in the volatile portions from the mixture. After the evaporation of volatile portions the oily residue was dissolved in MeOH and poured into diethyl ether to separate the residue again. The purified residue was dried and determined as formic acid ester derivative **2**: ^1H NMR (mixed solvent of Me_2SO-d_6 and $CDCl_3$) δ 2.47 ($C(O)CH_2CH_2C(O)$, 4 H), 3.0–3.7 ($NCH_2 + NCH_2CH_2O$, 6 H), 4.02 (t, CO_2CH_2, 2 H), 4.75 (s, OH, 1 H), 7.6 (br, NH, 2 H), 7.95 (s, NCHO, 1 H); IR 1730 ($\nu_{C=O}$ of ester), 1655 cm^{-1} ($\nu_{C=O}$ of amide). Anal. Calcd for $C_9H_{16}N_2O_5 \cdot H_2O$: C, 43.20; H, 7.25; N, 11.19. Found: C, 43.16; H, 7.40; N, 10.93.

Bicyclic Adduct 3. A mixture of OZO and GAn (10 mmol each) in 10 mL of acetonitrile was stirred at 0 °C under nitrogen. After several minutes a white solid precipitated. Then the solid was seperated, washed with CH_2Cl_2 4 times, and dried in vacuo to give 1.73 g of **3** (93% yield). Adduct **3** is very hygroscopic. IR, elemental analysis, and melting point data are given in the Results and Discussion.

Hydrolysis of 3. To a suspension of **3** (2.0 mmol) in acetonitrile, water (4 mmol) was added at room temperature. The hydrolysis reaction occurred exothermically and finished within a few minutes. After volatile portions of acetonitrile and excess water were evaporated from the homogeneous reaction mixture, a very viscous liquid was obtained. The liquid was purified by pouring an acetonitrile solution of the liquid into diethyl ether to separate the liquid again. This purification procedure was repeated 3 times (0.37 g, 90% yield). The liquid was determined to be an ester derivative of formic acid **4**: ^1H NMR (CD_3CN) δ 1.5–2.5 (m, $C(O)CH_2CH_2CH_2C(O)$, 6 H), 3.30 (q, NCH_2, 2 H), 4.04 (t, CO_2CH_2, 2 H), 6.63 (br, NH, 1 H), 7.89 (s, HCO_2, 1 H); IR 1720 ($\nu_{C=O}$, ester), 1640 cm^{-1} ($\nu_{C=O}$, amide). Anal. Calcd for $C_8H_{13}NO_5$: C, 47.29; H, 6.45; N, 6.89. Found: C, 47.35; H, 6.61; N, 7.01.

Polymerization of 3. In 1.2 mL of acetonitrile 0.57 g (3.1 mmol) of solid **3** was suspended under nitrogen and kept at 80 °C for 56 h. During the reaction the system gradually turned homogeneous. After the reaction the mixture was poured into 50 mL of diethyl ether to precipitate the polymeric material. The reprecipitation procedure using chloroform (good solvent) and diethyl ether (poor solvent) was repeated to give polymer **1b** (no. 9 in Table I). From the diethyl ether solution 0.16 g of GAn (1.4 mmol, 91% yield) was recovered.

Measurements. ^1H NMR spectra were recorded on a 60-MHz Hitachi R-20B NMR spectrometer at 35 °C with Me_4Si in organic solvents and with sodium 3-(trimethylsilyl)propionate standard in water solvent. The molecular weights of the copolymers were measured by vapor pressure osmometry in DMF at 55 °C or in chloroform at 35 °C. The IR measurements were carried out on a Hitachi Model EPI-G3 grating IR spectrophotometer. A melting point was measured in a capillary under nitrogen and was uncorrected.

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Cationic Ring-Opening Isomerization Polymerization of 2-[*p*-(Substituted)phenyl]-2-oxazolines. Effects of the Substituent on the Reactivities

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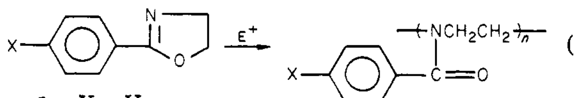
ABSTRACT: Five 2-[*p*-(substituted)phenyl]-2-oxazoline monomers (**1a–e**) were prepared, the substituents being H (**1a**), CH_3 (**1b**), OCH_3 (**1c**), Cl (**1d**), and NO_2 (**1e**). It was found that these five monomers were polymerized with the cationic initiator MeOTs to give polymers **2** via ring opening with isomerization. In order to examine the effects of the substituent on the nucleophilic reactivity of the monomer (reflected by k_i values) and on the polymerizability (reflected by k_{pn} values), the polymerization kinetics were carried out with **1a**, **1c**, and **1d** by means of ^1H NMR spectroscopy. From the substituent effects on both reactivities it was concluded that the polymerizability of monomer **1** was predominantly governed by the ring-opening reactivity of the corresponding oxazolinium propagating end. The latter reactivity was independently examined in terms of the substituent effect by a model reaction (reaction 14). Hammett plots of reaction 14 as well as propagation reaction 4 were well correlated with σ^+ values of the substituents X. The effect on the reactivities of the substituent at the 2 position of the oxazoline ring was also mentioned.

Cyclic imino ethers are well-known to undergo cationic ring-opening isomerization polymerizations as well as copolymerizations with various comonomers.[1] Resulting polymers of poly(*N*-acylalkylenimines) from the isomerization polymerizations of cyclic imino ethers are good starting polymers leading to linear poly(alkylenimines).[2]

Previously, we have reported kinetic studies on cationic ring-opening polymerizations of cyclic imino ethers, e.g., unsubstituted[3] and 2-methyl-2-oxazolines[4] and unsubstituted, 2-methyl-, and 2-phenyl-5,6-dihydro-4*H*-1,3-oxazines.[5] In these systems cationic initiators such as methyl tosylate (MeOTs) and methyl iodide have mainly been employed. Kinetic studies of the isomerization polymerization of 2-phenyl-2-oxazoline (PhOZO) have been performed with BF_3[6] and $HClO_4$ catalysts.[7] In these studies, however, kinetic conditions such as catalyst and solvent are different from those of our studies[3-5] and hence, it was difficult to correlate the reactivities of the various monomers on a similar basis. The present paper describes the ring-opening isomerization polymerization of 2-[*p*-(substituted)phenyl]-2-oxazolines by cationic initiators and the substituent effects on the reactivities.

Results and Discussion

Polymerization of 2-[*p*-(Substituted)phenyl]-2-oxazolines. First, five 2-[*p*-(substituted)phenyl]-2-oxazolines (**1a–e**) were prepared. The polymerization of **1** with a cationic initiator gives poly(*N*-[*p*-(substituted)benzoyl]ethylenimine) (**2**) as already known.[1] Table I shows the polymerization results of the five monomers (**1a–e**) and some data for the resulting polymers (**2a–e**). All these polymers are white powdery materials except for **2e**, which is a pale-yellow powder. The melting points (Table I) and solubilities (Table II) of the polymers are affected by the substituent. The molecular weights of **2a** and **2b** were 4100 and 4300, respectively, but those of **2c–e** could not be


(1)

1a, X = H
b, X = CH_3
c, X = OCH_3
d, X = Cl
e, X = NO_2

2a, X = H
b, X = CH_3
c, X = OCH_3
d, X = Cl
e, X = NO_2

Table I
Polymerization of 1 with MeOTs Initiator[a] and Molecular Weight, Melting Point, and IR Data of Polymer 2

	polymer				
monomer	conv, %	structure	mol wt[b]	mp, °C	IR (KBr), cm^{-1}
1a	97	2a	4100	136-138	1630 (amide)
1b	91	2b	4300	138-140	1630 (amide)
1c	94	2c		229-232	1630 (amide) 1250 (C—O—C)
1d	99	2d		268-270	1635 (amide) 760 (C—Cl)
1e	99	2e		245-250	1638 (amide) 1525 (Ar—NO_2) 1353 (Ar—NO_2)

[a] Polymerization conditions: $[1]_0$ = 6.0 mol/L in CH_3CN and $[MeOTs]_0$ = 4 mol % for $[1]_0$ at 105 °C for 10 h. [b] Determined by vapor pressure osmometry in DMF at 55 °C.