Ring-Opening Isomerization Polymerization of Cyclic Iminocarbonates

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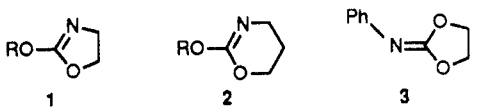
ABSTRACT: Five- (1) and six-membered cyclic iminocarbonates (2) having primary or secondary alkoxy substituents were newly prepared and the cationic ring-opening polymerization of them was examined. The polymerization of 2-ethoxy-2-oxazoline (**1a**) with methyl trifluoromethanesulfonate proceeded smoothly at 20 °C and yielded poly[[*N*-(ethoxycarbonyl)imino]ethylene] (**4a**) in a high yield, although the degree of polymerization was around 10 due to the chain transfer involving the 2-ethoxy substituent of the propagating species. The chain transfer was suppressed in the polymerization of 1 having a bulky alkoxy group, e.g., 2-(neopentyloxy)-2-oxazoline (**1e**). The reaction of **1a** with a catalytic amount of alkyl halide, on the other hand, yielded no polymeric product but an isomerized product, 3-ethyl-2-oxazolidone, instead. The mechanisms for polymerization, chain transfer, and isomerization were discussed and the ring-opening polymerizabilities of 2-isopropoxy-2-oxazoline (**1b**) and 2-isopropoxy-5,6-dihydro-4*H*-1,3-oxazine (**2b**) were compared with those of their 2-methyl homologues on the basis of kinetic results.

Introduction

Polymerizations of the family of cyclic imino ethers have aroused much interest in polymerization chemistry as well as in material science of functional polymers. Derivatives of 2-oxazoline and 5,6-dihydro-4*H*-1,3-oxazine have been known to produce poly[(*N*-acylimino)oligomethylene]s of low polydispersity in high yields by cationic ring-opening isomerization polymerization with a variety of cationic initiators such as an alkyl halide or alkyl sulfonate.[1,2] The hydrophilicity and lipophilicity of the produced polymers are easily controlled by the choice of the 2-substituent on the monomer and/or by the block copolymerization between the monomers. The amphiphilic property of these homo- and copolymers has been applied as antielectrostatic reagents,[3] hydrogels,[4] nonionic surfactants,[5,6] a surface modifier to commodity polymers,[7] and a chemical modifier for an enzyme.[8]

In spite of the wide application of these polymers, the possible variation of 2-substituent on the monomers has been so limited. Except for our recent study concerning cyclic pseudoureas, which have a 2-dialkylamino substituent,[9,10] the possible selection of 2-substituents was basically alkyl, aryl, alkenyl, or hydrogen (unsubstituted).[1]

In the present paper we describe the preparation and the polymerization of 2-alkoxy-2-oxazolines (1) and 2-alkoxy-5,6-dihydro-4*H*-1,3-oxazines (2). Since cyclic imino ether (or imidate) is the name for an ester of imidic acid, a N=C(R)O compound, in which R is hydrogen or carbon atom, these alkoxy derivatives should be categorized into another class, cyclic iminocarbonate, an analogue of carbonate having C=N instead of C=O. Although the ring-opening polymerization of the other type of cyclic iminocarbonate, **3**, has been reported by Mukaiyama et al.,[11] 1 and 2 have been quite unknown in the field of polymer chemistry. In the present paper the ring-opening polymerizability of these new cyclic monomers is also discussed in comparison to their 2-alkyl analogue, 2-methyl-2-oxazoline and 2-methyl-5,6-dihydro-4*H*-1,3-oxazine.



Results and Discussion

Preparation of Cyclic Iminocarbonates. Two cyclic iminocarbonates having a 2-ethoxy group, 2-ethoxy-2-oxazoline (**1a**) and 2-ethoxy-5,6-dihydro-4*H*-1,3-oxazine (**2a**), were prepared for the first time by the O-alkylation of the corresponding cyclic urethanes using the Meerwein reagent in dichloromethane at room temperature and subsequent neutralization (Scheme I).[12] A similar alkylation using trimethyloxonium fluoroborate for the preparation of 2-methoxy-2-oxazoline failed due to the poor solubility of this salt. A weaker electrophile than the Meerwein reagent, even methyl trifluoromethanesulfonate, was not nucleophilic enough to perform regioselective O-alkylation of the cyclic urethanes, ambident nucleophiles. Therefore, the synthetic route described in Scheme I was applicable only for the preparation of 2-ethoxy derivatives.

Cyclic iminicarbonates having other substituents were prepared by a newly found base-catalyzed alkoxy exchange reaction of **1a** or **2a** with a variety of alcohols as shown in Scheme II. This reaction required a somewhat severe condition and was carried out at 160 °C in mesitylene.

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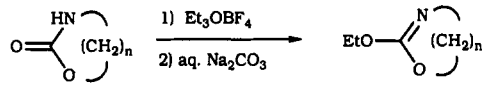
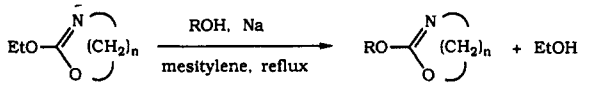
Scheme I



1a, n = 2; 86 % yield
2a, n = 3; 49 % yield

Scheme II



1a, n = 2
2a, n = 3

1b, n = 2; R = isopropyl
1c, n = 2; R = butyl
1d, n = 2; R = cyclohexyl
1e, n = 2; R = neopentyl
2b, n = 3; R = isopropyl

Table I
Preparation of Cyclic Iminocarbonates by the Alkoxyl Exchange Reaction

2-ethoxy compound	alcohol	[1a]/[Na]	[alcohol]/[1a]	time, h	iminocarbonate structure	iminocarbonate yield, %
1a	isopropyl	4	6	12	1b	98
1a	*n*-butyl	23	6	4	1c	50
1a	cyclohexyl	5	6	12	1d	53
1a	neopentyl	4	3	36	1e	10
2a	isopropyl	4	6	36	2b	78

Brønsted acids such as *p*-toluenesulfonic acid showed no significant effect on the exchange reaction.

Four five-membered cyclic iminocarbonates having primary or secondary alkoxy substituents, i.e., 2-isopropoxy-2-oxazoline (**1b**), 2-butoxy-2-oxazoline (**1c**), 2-cyclohexyloxy-2-oxazoline (**1d**), and 2-neopentyloxy-2-oxazoline (**1e**) and one six-membered monomer, 2-isopropoxy-5,6-dihydro-4*H*-1,3-oxazine (**2b**), were prepared by this method.[13] The results are summarized in Table I. The introduction of a *tert*-butoxy group at the 2-position failed, probably due to the steric bulkiness of the alkoxide anion.

Ring-Opening Polymerization of 1a. Although cyclic imino ethers have been known to polymerize by a variety of cationic initiators, i.e., Brønsted acids, Lewis acids such as boron trifluoride etherate, sulfate and sulfonate esters, and alkyl halides. Among these initiators the last two are most commonly used in recent years. Therefore, the ring-opening polymerization of **1a** was examined by using methyl trifluoromethanesulfonate (triflate) (MeOTf), methyl *p*-toluenesulfonate (tosylate) (MeOTs), benzyl chloride, and methyl iodide as initiators. Table II summarizes the polymerization results. The polymerization of **1a** with MeOTf proceeded smoothly even at 0 °C in aprotic polar solvents. This is in a good contrast to the fact that the polymerizations of cyclic imino ethers and cyclic pseudoureas usually proceed above 60 °C.[2,9] The structure of the resulting polymer was identified as poly[(*N*-(ethoxycarbonyl)imino)ethylene] (**4a**) from ^{1}H NMR and IR spectroscopies (Scheme III). Among aprotic polar solvents we examined, i.e., nitromethane, acetonitrile, and benzonitrile (run 1–3 in Table II), nitromethane gave the best results for the polymerization of **1a**, the highest polymer yield, the lowest molecular weight distribution, and the highest molecular weight under a similar condition: in these runs the initial feed ratios of the monomer to initiator were set around 10. Therefore, nitromethane was used as solvent in further experiments. The yield of **4a** was not so high in the polymerization with MeOTs, reflecting its relatively low initiating ability in comparison with MeOTf (run 5). Very interestingly, with the alkyl halide initiator no polymerization of **1a** took place, but, instead, an isomerized product of **1a**, 3-ethyl-2-oxazolidone (**6a**), was isolated in 80% yield from the reaction mixture in run 7 (vide infra).

The polymerization of cyclic imino ethers has been known to proceed via a living-like mechanism and produce polymers of low polydispersity.[2] But, in the present system, a chain transfer reaction is susceptible since the feed ratio of monomer to initiator scarcely influenced on the molecular weight of **4a**. For example, the molecular weights of **4a** for runs 8 and 9 are almost the same, while the theoretical molecular weights are 3670 for run 8 and 10 300 for run 9, which are calculated from the feed ratios of monomer to initiator combined with the polymer yields on the assumption of a living mechanism. The molecular weight distribution of **4a** prepared with a high initiator feed ($[M]_0/[MeOTf]_0 \approx 10$) were narrow, which showed a high k_i/k_p ratio. On the other hand, the broader molecular weight distributions of **4a** in runs 8 and 9 also suggest the occurrence of chain transfer. No significant effect on the polymerization temperature was found on the molecular weight of **4a**, while the polymer yield decreased with lowering the temperature (runs 9–11).

Figure 1 shows the 200-MHz ^{1}H NMR spectrum of the polymer **4a** obtained in run 9. The peaks at δ 1.24 (**a**), 3.2–3.5 (**c**), and 4.11 (**b**) are respectively ascribed to the methyl, *N*-methylene, and *O*-methylene protons of the repeating [*N*-(ethoxycarbonyl)imino]ethylene units. Other peaks are due to end groups of **4a** and some of them are ascribed to a 2-oxazolidone-type group at the polymer terminating end: the peaks at δ 3.68 (**d**) and 4.30 (**e**) are ascribed to the methylene protons of the 2-oxazolidone ring, 4- and 5-positions, respectively. The presence of 2-oxazolidone moiety in **4a** was also confirmed by its IR spectrum. Two carbonyl stretching bands appeared in the spectrum: a strong band at 1692 cm^{-1} was ascribed to the linear urethane group in the main chain and a weak band at 1750 cm^{-1} to the terminal oxazolidone group. The chemical shifts and the carbonyl stretching frequency coincide well with those for 3-ethyl-2-oxazolidone (see the Experimental Section).

From Figure 1 the information concerning the initiating terminal group of the polymer can be also obtained. In addition to the signal due to the *N*-methyl protons derived from the initiator (δ 2.91, peak **f**), an extra triplet peak (**h**) is observed at δ 1.11, which is ascribed to the methyl protons of the *N*-ethylurethane group. The signal for the methylene protons of the *N*-ethylurethane group is overlapped by that for the *N*-methylene protons of the repeating main unit at δ 3.2–3.5.

The polymerization pathway of **1a** involving the chain transfer reaction, which goes well with the above spectroscopic data, is as follows. By the reaction between **1a** and MeOTf, for example, an oxazolinium-type propagating species, 2-ethoxy-3-methyl-2-oxazolinium triflate (**5a**), is produced as the initiation step (Scheme IV). This compound, **5a**, could actually be isolated by the reaction of **1a** with an excess amount of MeOTf as a pale brown liquid whose ionic structure was identified by ^{1}H NMR spectroscopy.

The presence of the oxazolinium-type end group in the isolated polymer could not be observed from ^{1}H NMR spectroscopy because the oxazolinium group readily hydrolyzed to the 2-oxazolidone and *N*-(2-hydroxyethyl)-urethane derivatives during workup. A model hydrolysis reaction using **5a** in aqueous Na_2CO_3 gave 3-methyl-2-oxazolidone and ethyl *N*-methyl-*N*-(2-hydroxyethyl)carbamate in a ca. 2:1 molar ratio.

Table II
Ring-Opening Polymerization of 1a

run	initiator	$[M]_0/[I]_0$	solvent	temp, °C	time, h	4a yield, %	4a M_n (GPC[a])	4a M_n (VPO)	4a M_w/M_n (GPC[a])	4a DP (GPC[a])	4a DP (VPO)
1	MeOTf	11.1	CD_3NO_2	20	12	85	1320	1230	1.12	11.2	10.4
2	MeOTf	11.2	CD_3CN	20	12	59	1310		1.16	11.1	
3	MeOTf	10.6	$C_6H_5NO_2$	20	12	66	1130		1.18	9.5	
4	MeOTf	9.7	CH_3NO_2	0	12	67	870		1.24	7.3	
5	MeOTs	12.3	CH_3NO_2	20	12	36	1560		1.40	13.3	
6	MeI	10.7	CH_3NO_2	20	12	0					
7	$PhCH_2Br$	4.5	$C_6D_5NO_2$	100	36	0[b]					
8	MeOTf	51.4	CH_3NO_2	20	12	62	2070	2310	1.50	17.7	19.8
9	MeOTf	102.9	CH_3NO_2	20	12	90	1950	1620	1.53	16.7	13.8
10	MeOTf	97.6	CH_3NO_2	10	12	59	1970		1.57	16.8	
11	MeOTf	95.5	CH_3NO_2	0	12	14	1700		1.44	14.5	

[a] With polystyrene calibration. [b] 3-Ethyl-2-oxazolidone was isolated in 80% yield.

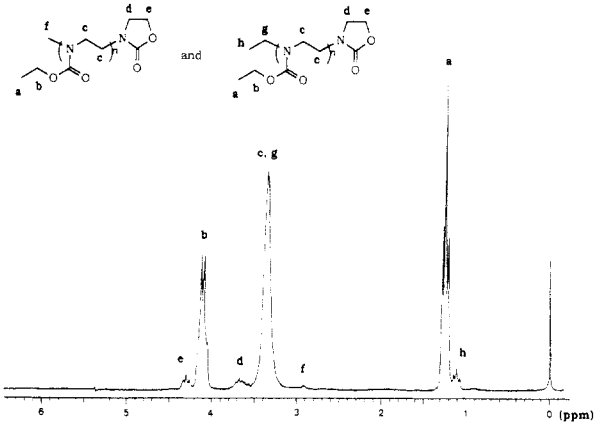
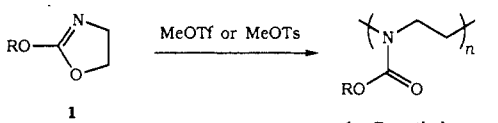


Figure 1. 200-MHz ^1H NMR spectrum of **4a** ($CDCl_3$).

Scheme III



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4a, R = ethyl
4b, R = isopropyl
4c, R = butyl
4d, R = cyclohexyl
4e, R = neopentyl

The propagation is an S_N2 type nucleophilic attack of the monomer to **5a**, which regenerates another oxazolinium-type propagating species, and the continuation of a similar propagation produces poly[[*N*-(ethoxycarbonyl)-imino]ethylene] (**4a**). The intermediacy of oxazolinium ions in the polymerization was confirmed from the comparison of the in situ ^1H NMR spectrum of the reaction mixture (run 1 in Table II) with that of **5a**.

The cationic charge on these oxazolinium propagating species, **5a**, for example, is stabilized by the contribution of four tautomers (see Scheme IV). The contributions of the first three tautomers, ammonium, *endo*-oxonium, and carbenium ion-type ones, are common to those in 2-alkyl-2-oxazolinium salts. The additional contribution of the fourth *exo*-oxonium-type tautomer brings an extra reactivity to **5a** and the propagating species: it is the good leaving ability of the *exo*-alkyl substituent. The nucleophilic attack of **1a** to this *exo*-methylene group of the propagation species results in the formation of a 2-oxazolidone group at the terminating end, and the by-produced 3-ethyl-2-ethoxy-2-oxazolinium triflate reinitiates the polymerization, which forms the polymer having an *N*-ethyl substituent at the initiating end. This chain transfer reaction is unique to cyclic iminocarbonate and no similar reaction has been known for cyclic imino ethers and pseudoureas.[29] The degrees of polymerization of **4a** in the runs with high $[M]_0/[I]_0$ ratios, 14 (run 8) and 20 (run 7), can be considered to reflect the relative reactivities of *endo*- and *exo*-methylene groups of the growing oxazolinium end, directly.

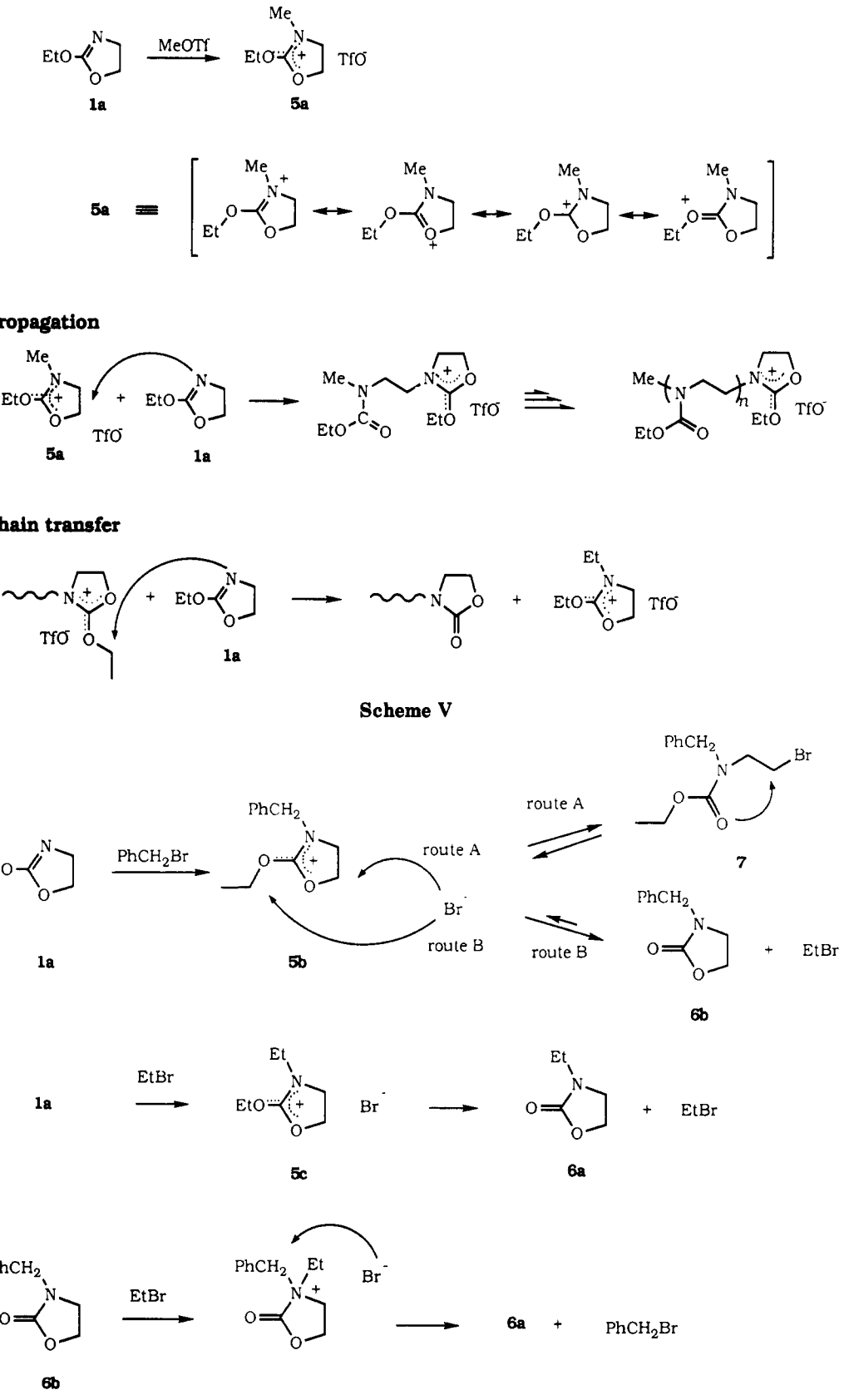
Mechanism for the Isomerization of 1a to 3-Ethyl-2-oxazolidone (6a) Catalyzed by Alkyl Halides. With alkyl halide initiator, methyl iodide or benzyl bromide, no polymerization of **1a** took place, instead, the isomerization of **1a** and **6a** occurred. The reaction mechanism is considered as follows. By the reaction of **1a** with benzyl bromide, for example, an oxazolinium species, 2-ethoxy-3-benzyl-2-oxazolinium bromide (**5b**), will be formed by the *N*-alkylation of **1a** in a similar manner (see Scheme V). But the counteranion, bromide, is much more nucleophilic than sulfonate ions, and, thus, it will attack the oxazolinium ring to yield a covalent urethane species, ethyl *N*-(2-bromoethyl)-*N*-methylcarbamate (**7**). We have no concrete evidence for the formation of these intermediates, but it is highly likely by analogy to the polymerization chemistry of cyclic imino ethers.[1,2,13,14] When bromide anion attacks the *exo*-methylene moiety of the oxazolinium ion, 3-benzyl-2-oxazolidone (**6b**) is produced. The by-produced ethyl bromide attacks the unreacted monomer to yield the other type of oxazolinium species, 2-ethoxy-3-ethyl-2-oxazolinium bromide (**5c**), and the subsequent exo-attack of bromide ion to **5c** yields *N*-ethyl-2-oxazolidone, **6a**, in a similar manner.

This potent reactivity of the *exo*-methylene group in **5** is the principle reason for the isomerization of **1a** to **6a** in the presence of alkyl halide. However, it is insufficient to explain the complete isomerization of **1a** without forming by-produced oligomers because the relative reactivity of *endo*- and *exo*-methylene groups will be little influenced by the nature of nucleophile. The existence of covalent species in the system will alter the rate of polymerization but does not much change the molecular weight of the produced polymer after the complete monomer consumption.

The quantitative isomerization of the monomer to **6a** is explained only on the assumption of a rapid equilibrium between the ionic and covalent type species: **5b** is reproduced from **7** by the attack of the urethane carbonyl oxygen to the halomethylene carbon. If the interconversion between these species occurs much more rapid than the attack of the monomer to **5b** or **7**, the pathway from **5b** to **6b**, which takes place occasionally and almost irreversibly, finally transforms the oxazolinium salt to oxazolidone, completely. The by-produced ethyl halide attacks **1a** to yield **6a** and, after that, a similar isomerization goes on. Consequently, all **1a** molecules isomerized to **6a** and **6b**.

If the above mechanism were appropriate, we will obtain a mixture of **6a** and **6b**, in which the latter's content

Scheme IV



Scheme V

depends on the initial monomer to initiator feed ratio. Contrary to these conjectures, we could not isolate **6b**, though the initial feed ratio, $[M]_0/[I]_0$, was 5.0. Therefore, we should postulate one more isomerization scheme from **6b** to **6a** to complete the mechanism, an alkyl exchange reaction between **6b** and **6a** via a quaternary ammonium species.

Ring-Opening Polymerization of Other Five-Membered Cyclic Iminocarbonates. The ring-opening polymerizations of other 5-membered cyclic iminocarbonates **1b–e** with MeOTf were also carried out in nitromethane at 20 °C with changing the feed ratio of monomer to initiator from ca. 10 to 100. The results are summarized in Table III. The resulting polymers, poly[[*N*-(isopro-

Table III
Ring-Opening Polymerization of 1 with MeOTf[a]

run	monomer	$[M]_0/[I]_0$	structure	yield, %	polymer				
					M_n (GPC[b])	M_n (VPO)	M_w/M_n (GPC[b])	DP (GPC[b])	DP (VPO)
1	**1b**	10.8	**4b**	88	1670	1560	1.17	12.7	11.8
2	**1b**	45.9	**4b**	98	4830		1.43	37.1	
3	**1b**	100	**4b**	77	5260	3660	1.80	40.5	28.1
4	**1c**	10.0	**4c**	82	1830	1370	1.22	12.6	9.3
5	**1c**	37.3	**4c**	89	3120	2120	1.36	21.6	14.6
6	**1c**	100	**4c**	75	4680	3240	1.43	32.5	22.4
7	**1d**	11.6	**4d**	87	1770	1610	1.13	11.1	10.0
8	**1d**	50.2	**4d**	90	4650	4420	1.42	29.4	27.9
9	**1d**	108	**4d**	88	8150	7930	1.55	51.6	50.2
10	**1e**	9.5	**4e**	85	2640	1660	1.16	15.4	9.6
11	**1e**	62.2	**4e**	80	9780	5260	1.18	57.4	30.9
12	**1e**	112	**4e**	75	17600	7760	1.17	103.8	45.7

[a] In nitromethane at 20 °C for 12 h. [b] With polystyrene calibration.

Table IV
Ring-Opening Polymerization of 2 with MeOTf[a]

run	monomer	$[M]_0/[I]_0$	solvent	time, h	polymer					
					structure	yield, %	M_n (GPC[b])	M_n (VPO)	M_w/M_n (GPC[b])	DP (GPC[b])	DP (VPO)
1	**2a**	9.8	CH_3NO_2	12	**8a**	35	780		1.20	5.8	
2	**2a**	10.0	CH_3NO_2	120	**8a**	62	860		1.51	6.4	
3	**2a**	52.2	CH_3NO_2	120	**8a**	56	850		1.55	6.3	
4	**2a**	94.4	CH_3NO_2	120	**8a**	29	910		1.56	6.8	
5	**2a**	10.5	$C_6H_5NO_2$	120	**8a**	76	1250		1.21	9.4	
6	**2a**	53.8	$C_6H_5NO_2$	120	**8a**	49	1460	1210	1.38	11.1	9.1
7	**2b**	9.4	$C_6H_5NO_2$	120	**8b**	77	1580	1520	1.19	10.8	10.4
8	**2b**	48.9	$C_6H_5NO_2$	120	**8b**	66	5540	3500	1.52	38.5	24.2

[a] At 20 °C. [b] With polystyrene calibration.

poxycarbonyl)imino]ethylene] (**4b**) from **1b**, poly[[*N*-(butoxycarbonyl)imino]ethylene] (**4c**) from **1c**, poly[[*N*-[(cyclohexyloxy)carbonyl]imino]ethylene] (**4d**) from **1d**, and poly[[*N*-[[2,2-(dimethylpropyl)oxy]carbonyl]imino]-ethylene] (**4e**) from **1e** were white semisolid or white powdery solid depending on their molecular weight. The polymer yields were generally high and no significant influence of the 2-substituent on the yields was observed in these runs. On the other hand, the 2-substituent influenced considerably on the molecular weight. A similar chain transfer reaction was observed for **1c** having a primary alkyl substituent. The presence of a 2-oxazolidone group at the terminating end of **4c** was confirmed from ^1H NMR spectroscopy.[15] But, as far as we can judge from the degree of polymerization of **4c**, the chain transfer occurs less frequently than for **1a**. In the polymerizations of **1b** and **1d** having secondary alkyl substituents and **1e** having a bulky neopentyl substituent the contribution of chain transfer became minor, and, especially, polymers of narrow molecular weight distribution (<1.2) were obtained from **1e**. The order of ease of chain transfer in these monomers, **1a** > **1c** > **1b** ≈ **1d** > **1e**, well coincides with that of average relative S_N2 rates for alkyl substrate in the monomers, i.e., ethyl (1) > butyl (0.4) > isopropyl (0.025) > neopentyl (10^{-5}),[16] which clearly indicates the chain transfer reaction is caused by the S_N2-type attack of the monomer to the *exo*-methylene group at the propagating end.

Polymerization of Six-Membered Cyclic Iminocarbonates 2. The 6-membered cyclic iminocarbonates, **2a** and **2b**, also underwent ring-opening polymerization with MeOTf and the structures of the resulting polymers were identified respectively as poly[[*N*-(ethoxycarbonyl)imino]-trimethylene] (**8a**) and poly[[*N*-(isopropoxycarbonyl)-imino]trimethylene] (**8b**) from IR and ^1H NMR spectroscopies. The results are summarized in Table IV. The polymerizability of **2** is significantly lower than that of its five-membered homologue. For example, the polymerization of **2a** with 10 mol % of MeOTf at 20 °C for 12 h afforded **8a** in 35% yield, while that of **1a** under the same condition yielded **4a** in 85% yield. The yield of **8a** increased to 62% when the reaction time was prolonged to 120 h. A similar tendency was also observed between the polymerizations of **2b** and **3b**. The low polymerizability of six-membered cyclic iminocarbonates in comparison with their five-membered homologues is reasonably ascribed to their poor ring strain (vide infra). As for a series of cyclic imino ethers, quite analogously, no six-membered one, as far as its polymerization has ever been investigated, shows higher polymerizability than its corresponding five-membered homologue.[1,10,13,14]

The molecular weights of **8a** prepared in nitromethane as solvent were also independent of the initial feed ratio, supporting the frequent chain transfer, and were generally lower than those of **4a**. Obviously, the decreased polymerizability of **4a**, i.e., the decreased reactivity of *endo*-methylene group of the oxazinium-type propagating species, increases the relative reactivity of the *exo*-methylene (or methyne for **4b**) group, which results in the frequent chain transfer. The polymerization of **2** in nitrobenzene gave better results than in nitromethane. The molecular weights of **8a** and **8b** prepared in nitrobenzene are comparable to those of **4a** and **4b** prepared in nitromethane with similar feed ratios as shown in Tables III and IV.

The polymerization mechanism for **2a** is consider quite similar to that for **1a**. The intermediacy of oxazinium propagating species in the **2a** polymerization system was confirmed from its in situ ^1H NMR spectrum.[17] Figure 2 shows the ^1H NMR spectrum of the isolated polymer **8a** prepared in run 6 in Table IV, from which the presence of a six-membered cyclic urethane structure at the polymer end was confirmed. In addition to the signals due to the main structure of **8a**, which are shown in Figure 2 and a, b, c, and d, peaks due to the perhydro-1,3-oxazin-2-one end group were observed at δ 2.05 (f), 3.35 (e), and 4.26 (g) and a triplet peak (j) ascribed to the methyl protons

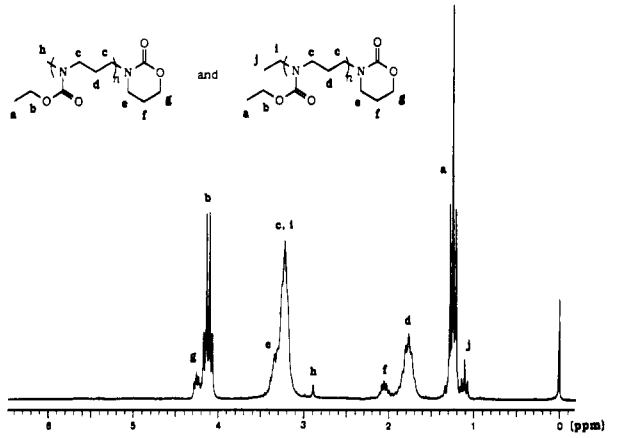


Figure 2. 200-MHz ^{1}H NMR spectrum of 8a ($CDCl_3$).

Table V
Rate Constants for the Ring-Opening Polymerization of the Family of Cyclic Imino Ethers and Their pK_a Values

monomer	initiator	$k_i \times 10^4$,[a] L/(mol·s)	$k_p \times 10^4$,[a] L/(mol·s)	k_p/k_i	pK_a[b]
1b	MeOTs[c]	0.058	280[i]	4800	5.4
1b	MeOTf[d]	>700	300[i]		
9	MeOTs[e]	1.1	0.98	0.89	5.5
2b	MeOTs[f]	1.3	3.2[i]	2.5	7.1
2b	MeOTf[g]	>700	3.6[i]		
10[h]	MeOTs	6.1	0.11	0.018	8.6

[a] In nitrobenzene-d_5 at 35 °C. [b] In water at 25 °C. [c] $[M]_0$ = 0.989 M; $[I]_0$ = 3.79 M. [d] $[M]_0$ = 0.407 M; $[I]_0$ = 0.0653 M. [e] $[M]_0$ = 3.66 M; $[I]_0$ = 0.73 M. [f] $[M]_0$ = 0.753 M; $[I]_0$ = 2.65 M. [g] $[M]_0$ = 0.202 M; $[I]_0$ = 0.0364 M. [h] Data from ref 29. [i] Without correction in due consideration of chain transfer.

of the initiating N-CH_2CH_3 end was observed at δ 1.10. The degree of polymerization of this 8a sample calculated from the integral ratio of the peak at δ 2.05 (end group) and 1.65–1.90 (main chain unit) was 10.3, which well coincides with those determined by GPC (11.1) and VPO (9.1).

Kinetic Study on the Polymerization of Cyclic Iminocarbonates. As described above, these five- and six-membered cyclic iminocarbonates have a higher polymerizability than the corresponding cyclic imino ethers. To elucidate the effect of 2-alkoxy substituent more clearly, kinetic studies were performed on the polymerizations of 1b and 2b with MeOTs and MeOTf.

The kinetic analyses on the above four polymerization systems were carried out on the basis of the direct determination of the instantaneous concentrations of propagating species, monomer, and initiator by means of ^{1}H NMR spectroscopy at 35 °C. The rate constants for initiation (k_i) and for propagation (k_p) were determined for each combination according to the procedure reported in the previous paper (see also the Experimental Section).[19] The data are shown in Table V. The initiation of cyclic iminocarbonates with MeOTf proceeded so fast that no exact rate constant could be obtained. The k_p values with two initiators are similar to each other for each of the monomers, although the k_p values with MeOTs initiator were less reliable than those with MeOTf since the polymerization with MeOTs proceeds via slow initiation followed by rapid propagation. Earlier kinetic studies on oxazoline derivatives have shown that the effect of the counterion on the k_p value is relatively small if the propagation proceeds via an ionic mechanism. The present work also supports this finding.

In these kinetic measurements the chain transfer constants k_c could not be directly determined since they were relatively low in comparison with k_p. Therefore, the k_p data shown in Table V were not corrected in due consideration of chain transfer. But, ratios k_c/k_p can be roughly evaluated from the computational simulation by using molecular weights of polymer prepared with a low initiator concentration, k_i, and k_p, which were ca. 1/35 for 1b and 1/40 for 2b. These values are considerably higher than those for 2-alkyl-2-oxazolines, 1/200 to 1/300.[29]

The in situ ^{1}H NMR measurement revealed that the propagating species in all these systems were ionic. Although the isolation of the 2-ethoxy-3-methyl-2-oxazolinium tosylate failed due to its high reactivity and the contamination of oligomeric byproducts, its ionic structure was confirmed from the in situ ^{1}H NMR spectrum.[18] Since the initiation is the nucleophilic attack of monomer to initiator, MeOTs, for example, we can directly evaluate the monomer nucleophilicity from the k_i value. The propagation is the attack of monomer to the propagating oxazolinium (or oxazinium) ion, the k_p value represents a combined effect of the monomer nucleophilicity and the ring-opening reactivity of the ionic propagating end. Thus, the ratio k_p/k_i can be used as an index for the ring-opening reactivity of the oxazolinium (or oxazinium) ion. In Table V the kinetic data for the polymerization of 2-methyl-2-oxazoline (9) and 2-methyl-5,6-dihydro-4*H*-1,3-oxazine (10) were also shown to discuss the influence of 2-substituent. From the comparison between the k_i values for 1b and 9 with MeOTs and between those for 2b and 10, it is obvious that the introduction of the 2-alkoxy substituent on the ring significantly decreases the nucleophilicity of monomer. This is in a good contrast to the effect of dialkylamino substituent, which enhances the nucleophilicity of oxazoline nitrogen.[20] The comparison of the pK_a values for the monomers also supports the electron-withdrawing effect of the alkoxy group. This unanticipated electron-withdrawing effect of the alkoxy group surprised us. However, an electron-withdrawing effect of the alkoxy group on carbonyl nucleophilicity has been well-known. Namely, methyl acetate (donor number, DN = 16.5[21]) is less nucleophilic than acetone (DN = 17), which in turn is less nucleophilic than *N*,*N*-dimethylacetamide (DN = 27.8). Moreover, the high carbonyl stretching frequency of ester (methyl acetate; $\nu_{C=O}$ = 1740 cm^{-1}) in comparison with that of ketone (acetone; 1710 cm^{-1}) has been explained by the fact that the inductive electron-withdrawing effect of alkoxy substituent overcomes its resonance electron-donating effect.[22]

The k_p for 1b is about 300 times as high as that for 9. This high polymerizability of 1b is ascribed to the high ring-opening reactivity of the oxazolinium ion derived from 1b as the k_p/k_i ratio clearly indicated. Obviously, the electron-withdrawing effect of the alkoxy substituent enhances the electrophilicity of the oxazolinium ion. This high ring-opening polymerizability of 1 in comparison with its 2-alkyl homologue 9 is interestingly compared with ring-opening reactivities of *exo*-imino cyclic compounds. Mukaiyama et al. have reported that the relative rates for the reactions of 3 and 2-(phenylimino)tetrahydrofuran, an exo-type cyclic imino ether, with carboxylic acids is 183:1. The rate-determining step in these reactions is also the attack of carboxylate anion on the protonated ionic species.[23]

The high k_p/k_i values for MeOTs also mean it is not a proper initiator for the polymerization of 1. The k_i for the 1b/MeOTf system was too fast to determine, but it was at least ten thousands times higher than the k_i for the 1b/MeOTs system. This agrees well with the reported

reactivity ratio of triflates to the corresponding tosylates, 4000–80 000.[24]

The six-membered iminocarbonate **2b** showed higher basicity and nucleophilicity and a lower ring-opening reactivity than the five-membered **1b**. A similar tendency is observed between imino ethers **9** and **10**. Therefore, the differences in reactivities are intrinsically derived from their ring size. Small-membered cyclic amines, e.g., aziridine, are generally less basic than linear or six-membered cyclic amines, e.g., piperidine, and it has been explained that the C–N bonds in small-ring amines have great p character than normal, leading to higher s character in the lone pair electrons. A lone pair with greater s character is less basic and nucleophilic.[25] The same explanation is also applicable to explain the high basicity and nucleophilicity of **2**. The low ring-opening reactivity of the six-membered oxazinium ion is ascribed to its low ring strain.

Cyclic imino ethers can be generally prepared from carboxylic acid derivatives and amino alcohols.[2] In the present paper we show cyclic iminocarbonates are prepared from alcohols and cyclic urethanes. Cyclic pseudoureas are from amines and cyclic iminocarbonates.[9] Therefore, it becomes possible to convert the three most common and important classes of compounds, carboxylic acids, alcohols, and amines, to oxazoline or oxazine derivatives. Although a vinyl functionality has been most commonly used to introduce a polymerizable group into a target molecule, we convince these oxazolinyl and oxazinyl groups will be other powerful candidates for this purpose.

Experimental Section

Materials. Triethyloxonium tetrafluoroborate was prepared according to the literature.[26] Perhydro-1,3-oxazin-2-one was prepared by the condensation between ethylene carbonate and 2-aminoethanol.[27] 2-Oxazolidone was purchased from Aldrich Chemical Co. and used as received. Other reagents and solvents were commercially available ones, which were dried by the conventional methods and distilled under nitrogen. The solvents were stored over molecular sieves 3 Å after distillation.

Measurements. ^{1}H NMR spectra were recorded on a 60-MHz Hitachi R-600 or a 200-MHz Varian Gemini-200 NMR spectrometer. ^{13}C NMR spectra were recorded on a Hitachi R-900 NMR spectrometer operated at 22.6 MHz. IR spectra were obtained on a Hitachi 260-50 infrared spectrometer. High-resolution mass spectra measured with a JEOL-MS-DX 300 and GC–MS measurements were carried out on a Shimazu GC MS QP2000. GPC analysis was performed by using a Shodex AC803 column in chloroform. Number-average molecular weights of the samples were measured by a vapor pressure osmometer (Corona Model 117) in chloroform at 35 °C.

Preparation of 2-Ethoxy-2-oxazoline (1a). Into a 3-L three-necked round flask equipped with a magnetic stirrer bar, a dropping funnel, a three-way stopcock, and a thermometer was introduced 142 g of 2-oxazolidone (1.63 mol) in 1.3 L of dichloromethane under nitrogen. The mixture was cooled to −10 °C in an ice–salt bath. Then 341 g of triethyloxonium tetrafluoroborate (1.79 mol) in 500 mL of dichloromethane was added dropwise to the solution with keeping the temperature of the mixture below 0 °C with stirring. After the addition, the mixture was stirred overnight at room temperature. Then the mixture was poured slowly into 2 L of ice-cooled saturated aqueous Na_2CO_3. The organic layer was separated and the aqueous layer was washed once with dichloromethane. The combined dichloromethane solution was dried over $MgSO_4$. After evaporation of the solvent, the residual crude **1a** was purified by distillation under a reduced pressure (41 °C/7.5 Torr). The yield was 92.9 g (50%). **1a**: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.34 (t, $|J|$ = 7.1 Hz, CH_3, 3 H), 3.81 (t, $|J|$ = 9.0 Hz, CH_2N, 2 H), 4.24 (q, $|J|$ = 7.1 Hz, CH_3CH_2, 2 H), 4.40 (t, $|J|$ = 9.0 Hz, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3), 51.7 (C_4), 65.6 (CCH_3), 68.3 (C_5), 162.3 (C=N); IR (neat) 2970 (ν_{C-H}), 1660 ($\nu_{C=N}$), 1380, 1320, 1260 cm^{-1}; mass spectrum, *m/e* 115 (M^+, 36), 88 (100), 87 (43), 86 (55), 57 (100), 55 (41); exact mass found, *m/e* 115.0621 (calcd for $C_5H_9NO_2$, *m/e* 115.0633).

2-Ethoxy-5,6-dihydro-4*H*-1,3-oxazine (2a) was similarly prepared from perhydro-1,3-oxazin-2-one in 49% yield. **2a**: colorless liquid; bp 48–50 °C/5 Torr; ^{1}H NMR ($CDCl_3$) δ 1.34 (t, $|J|$ = 7.0 Hz, CH_3, 3 H), 1.70–2.19 (m, C_5, 2 H), 3.37 (t, $|J|$ = 5.0 Hz, NCH_2, 2 H), 4.18 (q, $|J|$ = 7.0 Hz, *exo*-OCH_2, 2 H), 4.25(t, $|J|$ = 5.0 Hz, *endo*-OCH_2, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 21.5 (C_5), 41.3 (C_4), 62.2 (C_6), 65.8 (CCH_3), 153.5 (C=N); IR (neat) 2980 (ν_{C-H}), 1690 and 1675 (ν_{C-N}), 1335, 1365, 1160, 1040 cm^{-1}; mass spectrum, *m/e* 129 (M^+, 25), 102 (83), 101 (46), 85 (47), 84 (44), 74 (30), 56 (100); exact mass found, *m/e* 129.0799 (calcd for $C_5H_9NO_2$, *m/e* 129.0790).

General Procedure for the Alkoxy Exchange Reaction. In a 200-mL two-necked flask equipped with a reflux condenser and a magnetic stirrer bar were placed 5.0 mL of **1a** (46 mmol), 100 mL of mesitylene, and 26 mL of *n*-butanol (280 mmol). To the mixture was added 0.28 g of sodium (12 mmol) and the mixture was heated to 160 °C with stirring. The consumption of **1a** was traced by GLC and the almost complete conversion of **1a** was attained after 3.5 h. The reaction mixture was cooled to room temperature and poured into 200 mL of ice-cooled 0.3 N aqueous H_2SO_4 in a separating funnel, and the funnel was shaken quickly. The aqueous layer was immediately poured into 250 mL of ice-cooled 0.8 N aqueous NaOH. The basic aqueous solution was shaken twice with diethyl ether, and the combined ether layer was washed with saturated aqueous NaCl and dried over $MgSO_4$. After evaporation of the solvent, the residual product **1c** was purified further by distillation under a reduced pressure (81 °C/11 Torr). The yield was 3.31 g (23.1 mmol). **1c**: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, $|J|$ = 7.5 Hz, CH_3, 3 H), 1.15–1.98 (m, $CH_3CH_2CH_2$, 4 H), 3.88 (t, $|J|$ = 9.0 Hz, CH_2N, 2 H), 4.11–4.65 (m, CH_2O, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.8 (CH_3), 18.8, 30.6, 51.4 (C_4), 67.7 (C_5), 69.8, 161.5 (C=N); IR (neat) 2980 (ν_{C-H}), 1665 ($\nu_{C=N}$), 1410, 1330, 1270 cm^{-1}; mass spectrum, *m/e* 143 (M^+, 14), 88 (100), 87 (18), 57 (34), 56 (30); exact mass found, *m/e* 143.0940 (calcd for $C_7H_{13}NO_2$, *m/e* 143.0946).

1b: colorless liquid; bp 44–45 °C/8.5 Torr; ^{1}H NMR ($CDCl_3$) δ 1.28 (d, $|J|$ = 6.0 Hz, CH_3, 6 H), 3.78 (t, CH_2N, 2 H), 4.35 (t, CH_2O, 2 H), 4.83 (sept, $|J|$ = 6.0 Hz, CH, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 51.4 (C_4), 67.4 (C_5), 73.6 (CHO), 160.8 (C=N); IR (neat) 2990 (ν_{C-H}), 1670 ($\nu_{C=N}$), 1395, 1330, 1275 cm^{-1}; mass spectrum, *m/e* 129 (M^+), 88 (100), 87 (79), 59 (33); exact mass found, *m/e* 129.082 (calcd for $C_6H_{11}NO_2$, *m/e* 129.079).

1e: colorless liquid; bp 60 °C/0.1 Torr; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, CH_3, 9 H), 3.75 (t, CH_2N, 2H), 3.89 (s, *exo*-OCH_2, 2 H), 4.35 (t, *endo*-OCH_2, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.9 (CH_3), 32.5, 52.6 (C_4), 69.0 (C_5), 81.3, 163.5 (C=N); IR (neat) 2950 (ν_{C-H}), 1660 ($\nu_{C=N}$), 1480, 1410, 1380, 1340, 1320 cm^{-1}; mass spectrum, *m/e* 157 (M^+, 41), 144 (15), 89 (54), 71 (100); exact mass found, *m/e* 157.110 (calcd for $C_8H_{15}NO_2$, *m/e* 157.214).

2b: colorless liquid; bp 90 °C/20 Torr; ^{1}H NMR ($CDCl_3$) δ 1.24 (d, $|J|$ = 6.0 Hz, CH_3, 6 H), 1.90–2.10 (m, C_5, 2 H), 3.39 (t, $|J|$ = 6.0 Hz, C_4, 2 H), 4.25 (t, $|J|$ = 6.0 Hz, C_6, 2 H), 4.85 (sept, $|J|$ = 6.0 Hz, CHO, 1 H); IR (neat) 2990 (ν_{C-H}), 1690 and 1672 ($\nu_{C=N}$), 1360, 1270, 1150 cm^{-1}; mass spectrum, *m/e* 143 (M^+, 2), 102 (100), 85 (54), 74 (65); exact mass found, *m/e* 143.093 (calcd for $C_7H_{13}NO_2$, *m/e* 143.095).

Typical Procedure for the Ring-Opening Polymerization of Cyclic Iminocarbonates. In a test tube equipped with a magnetic stirrer bar and a three-way stopcock were placed 0.345 g (3 mmol) of **1a** and 2 mL of nitrobenzene under nitrogen. To the solution was added 4.44 mg (0.27 mmol) of methyl triflate with stirring and the mixture was stirred at 20 °C for 12 h. The produced polymer **4a** was isolated by precipitation from an equivolume mixture of diethyl ether and hexane, purified further by repeated reprecipitation from dichloromethane to the ether/hexane mixture, and dried in vacuo. The yield was 0.257 g (66 %). **4a**: ^{1}H NMR ($CDCl_3$) δ 1.25 (t, $|J|$ = 7.2 Hz, CH_3, 3 H), 2.91 (s, CH_3N at initiating end), 3.2–3.5 (brs, CH_2N, 4 H), 4.13 (q, CH_2O, 2 H); IR ($CHCl_3$) 2984 (ν_{C-H}), 1693 ($\nu_{C=O}$), 1484, 1427, 1240, 1210 cm^{-1}.

4b: ^{1}H NMR ($CDCl_3$) δ 1.22 (d, $|J|$ = 6.0 Hz, CH_3, 6 H), 2.89 (s, CH_3N at initiating end), 3.3–3.6 (brs, CH_2N, 4 H), 4.87 (sept,

$|J|$ = 6.0 Hz, CHO, 1 H); IR ($CHCl_3$) 2983 (ν_{C-H}), 1691 ($\nu_{C=O}$), 1475, 1425, 1242, 1207 cm^{-1}.

4c: ^1H NMR ($CDCl_3$) δ 0.92 (t, $|J|$ = 6.0 Hz, CH_3, 3 H), 1.17–1.93 (m, CH_2CH_2CO, 4 H), 2.89 (s, CH_3N at initiating end), 3.2–3.5 (brs, CH_2N, 4 H), 4.05 (t, $|J|$ = 6.0 Hz, CH_2O, 2 H); IR ($CHCl_3$) 2960 (ν_{C-H}), 1692 ($\nu_{C=O}$), 1469, 1427, 1218 cm^{-1}.

4d: ^1H NMR ($CDCl_3$) δ 0.50–2.30 (m, CH_2 protons in cyclohexyl ring, 10 H), 2.91 (s, CH_3N at initiating end), 3.2–3.6 (brs, CH_2N, 4 H), 4.07–4.83 (m, CH, 1 H); IR ($CHCl_3$) 3009, 2939, 1690 ($\nu_{C=O}$), 1473, 1425, 1222 cm^{-1}.

4e: ^1H NMR ($CDCl_3$) δ 0.92 (s, CH_3, 9 H), 2.93 (s, CH_3N at initiating end), 3.21–3.61 (brs, CH_2N, 4 H), 3.78 (s, CH_2O, 2 H); IR ($CHCl_3$) 2962 (ν_{C-H}), 1696 ($\nu_{C=O}$), 1218, 1204 cm^{-1}.

8a: IR ($CHCl_3$) 2987 (ν_{C-H}), 1688 ($\nu_{C=O}$), 1485, 1428, 1216 cm^{-1}.

8b: ^1H NMR ($CDCl_3$) δ 1.20 (d, $|J|$ = 6.0 Hz, CH_3, 6 H), 1.47–2.22 (m, CH_2CN, 2 H), 2.87 (s, CH_3N at initiating end), 2.9–3.6 (brs, CH_2N, 4 H), 4.90 (sept, $|J|$ = 6.0 Hz, CH, 1 H); IR ($CHCl_3$) 2981 (ν_{C-H}), 1684 ($\nu_{C=O}$), 1472, 1418, 1219 cm^{-1}.

Isolation of 2-Ethoxy-3-methyl-2-oxazolinium Triflate (5a). All operations were carried out under nitrogen. In a test tube equipped with a three-way cock and a magnetic stirrer bar were placed 0.856 g (5.22 mmol) of MeOTf and 0.6 mL of dichloromethane. The mixture was cooled with ice and 0.297 g (2.56 mmol) of **1a** was added slowly to the mixture with stirring. The mixture was kept at room temperature for 2 h and then diluted with 5 mL of diethyl ether to precipitate the crude **5a**, which was washed several times with diethyl ether and dried in vacuo. The yield was almost quantitative (0.720 g). The ionic structure of **5a** was determined from the comparison of its ^1H NMR spectrum with those of 2-alkyl-3-methyl-2-oxazolinium salts.[28] Hygroscopic pale brown liquid; ^1H NMR ($CDCl_3$) δ 1.47 (t, 3 H, OCH_2CH_3), 3.11 (s, 3 H, NCH_3), 4.11 (t, 2 H, NCH_2), 4.69 (q, 2 H, OCH_2CH_3), 5.07 (t, 2 H, OCH_2CH_2).

Isomerization of 1a to 3-Ethyl-2-oxazolidone. In a test tube equipped with a magnetic stirrer bar and the three-way stop cock were placed 0.314 g (2.73 mmol) of **1a** and 2 mL of nitrobenzene under nitrogen. To the solution was added 94.5 mg (0.55 mmol) of benzyl bromide with stirring and the mixture was maintained at 45 °C for 40 h. Then the mixture was poured into 50 mL of an equivolume mixture of diethyl ether and hexane to check the absence of polymeric product. After evaporation of solvents the residual solid was subject to distillation using a Kügelrohr to obtain the essentially pure 3-ethyl-2-oxazolidone. **6a**: clear liquid; 80% yield; bp 50 °C/1.2 Torr; ^1H NMR δ 1.12 (t, 3 H, CH_3), 3.25 (q, 2 H *exo*-NCH_2), 3.5–3.7 (m, 2 H, *endo*-NCH_2), 4.2–4.5 (m, 2 H, OCH_2). IR (neat) 2975, 2930, 1755 ($\nu_{C=O}$), 1430, 1265, 1055, 760 cm^{-1}; mass spectrum, *m/e* 115 (M^+, 43), 100 (60), 56 (100), 42 (23), 28 (31); exact mass found, *m/e* 115.0633 (calcd for $C_5H_9NO_2$, *m/e* 115.0633).

Kinetics. A typical procedure is as follows. In an NMR tube equipped with a three-way cock containing 0.0375 g of **2b** (0.262 mmol) dissolved in 0.576 mL of nitrobenzene-d_5 was added 0.0069 g of MeOTf (0.042 mmol) under nitrogen. Then the tube was sealed and kept at 35 °C. The progress of the reaction was monitored directly by ^1H NMR spectroscopy, and the instantaneous concentrations of the monomer (from the OCH_2 triplet at δ 4.25), the propagating oxazolinium species (from the $OCCH_3$ peaks at δ 1.52), and the polymer (from the NCH_2 broad peak at δ 3.4–3.7) were obtained directly from the integral intensity of the spectrum. The reaction system was homogeneous throughout the kinetic run.

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(15) Peaks ascribed to the terminal 2-oxazolidone end group were observed at δ 3.65 and 4.30 in the ^1H NMR spectrum of **4c** (run 6 in Table III). The presence of the 2-oxazolidone end group was also confirmed from ^1H NMR spectroscopy in a similar manner for **4b** and **4d**, but not for **4e**.

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(17) In the spectrum peaks ascribed to 2-ethoxy-3-methyl-5,6-dihydro-4*H*-1,3-oxazinium ion or the propagating oxazinium-type end group were observed at δ 3.07 (s, NCH_3), 4.6–4.9 (m, *exo*-OCH_2), and around 5.0–5.3 (m, *endo*–OCH_2).

(18) In the spectrum peaks ascribed to 2-ethoxy-3-methyl-2-oxazolinium tosylate or propagating oxazolinium-type end groups were observed at δ 1.44 (d, CH_3), 2.40 (s, CH_3Ar), 4.5–4.8 (m, *exo*-OCH_2), and around 5.0–5.2 (m, *endo*–OCH_2). Other peaks were weak or overlapped by peaks due to the unreacted MeOTs.

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Registry No. **1a**, 4075-55-2; **1a** (homopolymer), 143076-61-3; **1b**, 139602-24-7; **1b** (homopolymer), 143076-62-4; **1c**, 79493-65-5; **1c** (homopolymer), 143076-63-5; **1d**, 79493-74-6; **1d** (homopolymer), 143076-64-6; **1e**, 139602-25-8; **1e** (homopolymer), 143076-65-7; **2a**, 79493-70-2; **2a** (homopolymer), 143076-66-8; **2b**, 143076-57-7; **2b** (homopolymer), 143076-67-9; **5a**, 143076-59-9; **9**, 1120-64-5; **10**, 10431-93-3; *i*-PrOH, 67-63-0; BuOH, 71-36-3; $(CH_3)CCH_2OH$, 75-84-3; perhydro-1,3-2-oxaolidone, 497-25-6; perhydro-1,3-oxazin-2-one, 5259-97-2; cyclohexyl alcohol, 108-93-0; 3-ethyl-2-oxazolidone, 52611-18-7; benzyl bromide, 100-39-0.