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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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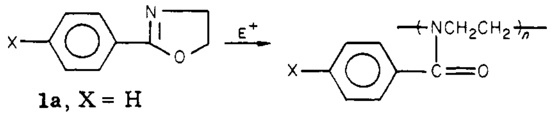
ABSTRACT: Five 2-[*p*-(substituted)phenyl]-2-oxazoline monomers (**1a–e**) were prepared, the substituents being H (**1a**), CH_3 (**1b**), OCH_3 (**1c**), Cl (**1d**), and NO_2 (**1e**). It was found that these five monomers were polymerized with the cationic initiator MeOTs to give polymers **2** via 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

monomer	polymer: conv, %	polymer: structure	polymer: mol wt[b]	polymer: mp, °C	polymer: 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.

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Table II
Solubility Data of Polymers 2a-e[a]

	CH_3CN	$CHCl_3$	DMF	Et_2O	n-C_6H_{14}
2a	S	S	S	I	I
2b	S	S	S	I	I
2c	I	P	I	I	I
2d	I	I	I	I	I
2e	I	I	I	I	I

[a] S = soluble, P = partially soluble, I = insoluble.

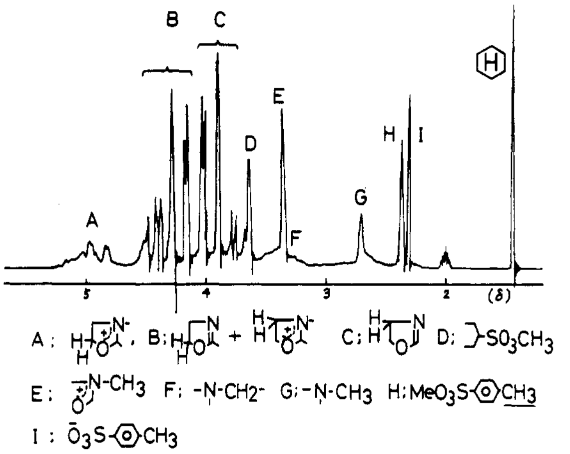
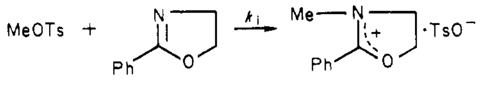


Figure 1. ^1H NMR spectrum of the polymerization system of **1a** with MeOTs catalyst at 100 °C in CD_3CN. $[\mathbf{1a}]_0 = 1.03$ mol/L and $[\mathbf{1a}]_0/[\mathrm{MeOTs}]_0 = 4.54$.

obtained due to their very low solubilities.

Kinetics of the Polymerization of 1 with MeOTs. The analysis of the polymerization kinetics was performed by ^1H NMR spectroscopy. Figure 1 shows the ^1H NMR spectrum of the early stage of the polymerization system with MeOTs initiator. The high concentration of MeOTs, 22 mol % for **1a**, made it possible to determine precisely the concentration of active species. The assignment of the signals is given in the figure. The active species of the polymerization system, shown by signals A and E, are observed as 2-oxazolinium salts. Therefore, the ring-opening isomerization polymerization of **1a** is represented by the following reactions:

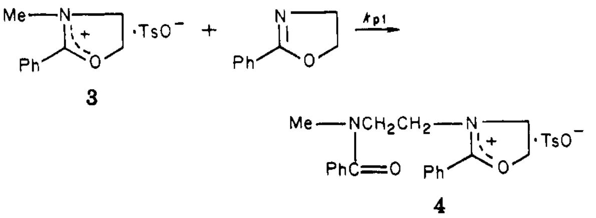
Initiation



(2)

1a **3**

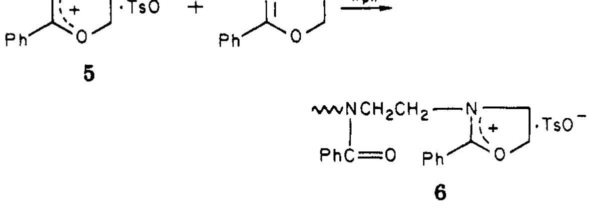
Propagation



3

(3)

4



5

(4)

6

The initiation reaction could be followed by the increase of peak I and the decrease of peak H; i.e.

$$[\mathrm{I}]_t = [\mathrm{I}]_0 \frac{H}{H + I} \tag{5}$$

where $[\mathrm{I}]_0$ and $[\mathrm{I}]_t$ denote, respectively, the initial and instantaneous concentrations of initiator and H and I are the integrated values of peaks H and I. The consumption of monomer could be monitored by the decrease of signal B. With the progress of polymerization, signal F, due to NCH_2 of the polymer, became larger, which overlapped with signals C, D, E, and G. Therefore, the instantaneous monomer concentration, $[\mathrm{M}]_t$, is given by

$$[\mathrm{M}]_t = [\mathrm{M}]_0 \left\{ \frac{2(B - A)}{(A + B + C + D + E + F + G) - (H + I)} \right\} \tag{6}$$

where $[\mathrm{M}]_0$ is the initial monomer concentration. The integration value of all signals was determined by comparison with that of an internal standard of cyclohexane signal at δ 1.44.

The consumption rates of initiator and monomer are given by the equations

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = k_i[\mathrm{I}][\mathrm{M}] \tag{7}$$

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_i[\mathrm{I}][\mathrm{M}] + k_p[\mathrm{P}^*][\mathrm{M}] \tag{8}$$

where k_i and k_p are the rate constants of initiation and propagation, respectively, and $[\mathrm{P}^*]$ represents the concentration of oxazolinium species such as **3** and **5**. The system was living and the following relationship was found to be held strictly:

$$[\mathrm{P}^*] = [\mathrm{I}]_0 - [\mathrm{I}] \tag{9}$$

Substitution of relationship 9 into eq 8 gives

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = (k_i - k_p)[\mathrm{I}][\mathrm{M}] + k_p[\mathrm{I}]_0[\mathrm{M}] \tag{10}$$

Integrated forms of eq 7 and 10 are

$$\ln \frac{[\mathrm{I}]_0}{[\mathrm{I}]} = k_i \int_0^t [\mathrm{M}]\, \mathrm{d}t \tag{11}$$

and

$$\frac{\ln \{[\mathrm{M}]_0/[\mathrm{M}]\}}{\int_0^t [\mathrm{I}]\, \mathrm{d}t} = (k_i - k_p) + k_p \frac{[\mathrm{I}]_0 t}{\int_0^t [\mathrm{I}]\, \mathrm{d}t} \tag{12}$$

Values of $\int_0^t [\mathrm{M}]\, \mathrm{d}t$ and $\int_0^t [\mathrm{I}]\, \mathrm{d}t$ were obtained by graphical integration. Thus, k_i and k_p values were calculated. For the propagation, two different values were obtained with the propagation rate constant of the first step (k_{p1} in reaction 3) and of the later steps (k_{pn}, $n \geq 2$ in reaction 4) (Table III). Similar results have been observed also in the polymerization kinetics of 2-methyl-2-oxazoline.[4]

Kinetic analysis was carried out at three different temperatures. Arrhenius plots of these three rate constants were all linear and the activation parameters of respective elementary reactions were obtained from them (Table III).

Similarly, kinetic analyses were performed with monomers **1c** and **1d** (Table III). Polymerization of monomer **1b** was examined by ^1H NMR spectroscopy but the kinetic analysis was not successful due to the overlapping of methyl signals. The polymerization kinetics of **1e** was not possible since the system was not homogeneous due to the reduced solubility of the monomer and the product polymer.

Effects of Substituent X of 1 on the Reactivities. For the three monomers examined the substituent effects on both the intitation and propagation rate constants are subtle. However, the trend of the effects is clearly shown. The cationic polymerizabilities of monomers **1a**, **1c**, and

Table III
Rate Constants and Activation Parameters in the Polymerization of Three 2-Oxazolines (**1a**, **1c**, and **1d**)

	$k_i \times 10^3$ [a]			$k_{p1} \times 10^3$ [a]			$k_{pn} \times 10^3$ [a]		
	X = H	X = OCH$_3$	X = Cl	X = H	X = OCH$_3$	X = Cl	X = H	X = OCH$_3$	X = Cl
T = 90 °C	0.59	0.78	0.31	0.50	0.33	0.52	0.53	0.43	0.65
T = 100 °C	1.04	1.43	0.49	0.83	0.71	1.10	1.25	0.79	1.42
T = 110 °C	1.83	2.92	0.95	1.55	1.17	2.25	2.88	1.93	3.36
ΔE, kcal/mol	15.7	18.3	15.5	15.7	17.6	20.3	23.5	20.8	22.8
A, L/(mol·s)	1.7×10^6	7.9×10^7	6.5×10^5	1.3×10^6	1.3×10^7	8.9×10^8	7.2×10^{10}	1.3×10^9	3.3×10^{10}

[a] L/(mol·s).

Table IV
Rate Constants of Ring-Opening Reaction of Five Onium Salts **7**[a] and Their Relative Values

	X of **7**				
	NO$_2$	Cl	H	CH$_3$	OCH$_3$
$k_{RO} \times 10^3$ [b]	3.4	1.0	0.78	0.43	0.26
$k_{RO(X)}/k_{RO(H)}$	4.4	1.3	1.0	0.55	0.33

[a] [**7**]/[**1a**] = 1.0/0.6 in CD$_3$CN at 100 °C. [b] L/(mol·s) at 100 °C.

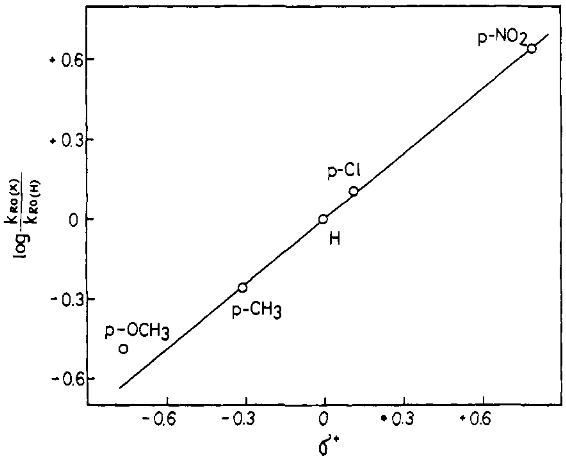
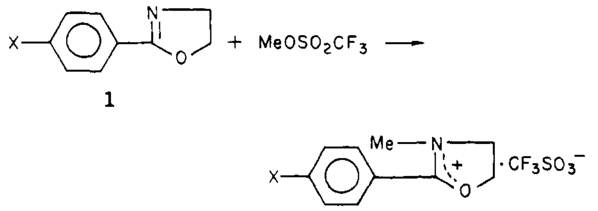


Figure 2. Hammett plots of log $\{k_{RO(X)}/k_{RO(H)}\}$ vs. σ^+ values.

1d reflected by k_{pn} values (e.g., reaction 4 are in the following order (shown by substituent): Cl > H > OCH$_3$. That is, an electron-withdrawing group such as chlorine enhanced the polymerizability and vice versa. It is believed that for cationic ring-opening polymerization, the polymerizability is mainly governed by two factors, namely, the ring-opening reactivity of the propagating oxazolinium species and the nucleophilicity of the monomer.[5,8] The k_i values can be taken to represent the nucleophilic reactivity toward a common electrophile of MeOTs, e.g., reaction 2. Therefore, the nucleophilicity of monomers is in the following order: OCH$_3$ > H > Cl. This order is quite reasonable since an electron-donating group such as methoxyl increased the nucleophilicity but is the reverse of that of polymerizability. These observations lead to a tentative conclusion that the order of polymerizability of monomer is determined predominantly by the ring-opening reactivity of the propagating end and hence the latter reactivity should be in the order Cl > H > OCH$_3$.

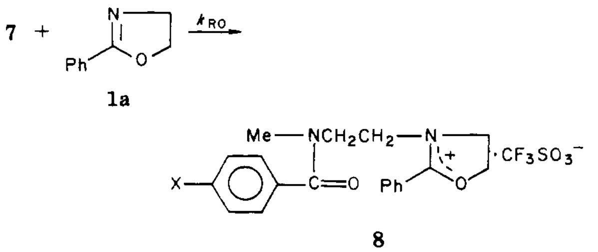
In order to shed more light on the reactivity of the propagating ring at the end to open, the following model reactions were examined. First, N-methyl-2-[p-(substituted)phenyl]-2-oxazolinium trifluoromethanesulfonate (**7**) was prepared in situ. It is known that the 1:1 molar reaction of an alkyl trifluoromethanesulfonate and a cyclic imino ether gives spontaneously an alkylated onium salt like **7**.[5a] **7** was quite stable under the reaction conditions.



1

7

(13)



1a

8

(14)

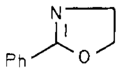
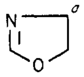
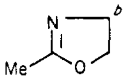
Then, **7** was caused to react with **1a** to give 1:1 reaction product **8**. Onium species **7** can be taken as a model of the propagating end. The reaction of **7** having various substituents X with a common nucleophile of **1a** represents the ring-opening reactivity of **7**. In reaction 14 the amount of **1a** was 60 molar % toward **7** to prevent the further reaction of **1a** with **8**. ^{1}H NMR spectroscopy was successfully applied for the kinetic analysis of reactions 13 and 14. Table IV shows the second-order rate constants of the ring-opening reaction (k_{RO} in reaction 14) of five onium salts **7** and the relative values ($k_{RO(X)}/k_{RO(H)}$). The order of k_{RO} values is NO$_2$ > Cl > H > CH$_3$ > OCH$_3$, which is the same as that of the polymerizability. The electron-withdrawing groups (NO$_2$ and Cl) destabilized the onium salt **7** and enhanced its ring-opening tendency whereas the electron-donating groups (OCH$_3$ and CH$_3$) stabilized **7** and reduced the reactivity of **7**.

Similar arguments can be extended to the ring-opening reactivity of the propagating end. As a conclusion, therefore, *the effects of the substituent X of* **1** *on the* reactivities are presented as follows: an electron-withdrawing group (e.g., X = Cl) reduced the nucleophilic reactivity of **1** but enhances the ring-opening reactivity of the propagating end, and the reverse situation is true for the case of an electron-donating group (e.g., X = OCH$_3$). As a whole, the polymerizability is governed by the reactivity of the propagating end.

Hammett Relationship. Figure 2 shows a Hammett plot based on the data in Table IV. The plot is better correlated with σ^+ values (ρ = 0.729, correlation coefficient R = 0.997) than with σ values (ρ = 0.942, R = 0.980).[9] This is quite reasonable since reaction 14 is the reaction of a cationic species **7** with a common nucleophile of a dipole **1a**.

Although only three data points each are available for both the initiation and propagation, a Hammett plot was attempted. From k_i data at 100 °C, a ρ value of −0.907 with σ values was obtained (R = 0.957). From k_{pn} data at 100 °C, ρ = 0.263 with σ^+ values (R = 0.994) and ρ = 0.541 with

Table V
Rate Constants and Activation Parameters in the Polymerization of 2-Oxazolines with MeOTs Initiator in CD_3CN

	 PhOZO	[a] OZO	[b] MeOZO
$k_i \times 10^4$, L/(mol·s)	$(0.16)^{c,e}$	0.98^c	1.82^c
$k_p \times 10^4$, L/(mol·s)	12.5^d $(0.02)^{c,e}$	$(13\,000)^{d,e}$ 19^c	$(120)^{d,e}$ 1.17^c
ΔE_p, kcal/mol	23.5	25	19.1
A_p, L/(mol·s)	7.2×10^{10}	7.5×10^{14}	1.9×10^9

[a] Reference 3. [b] Reference 4a. [c] At 40 °C. [d] At 100 °C. [e] Calculated value from the experimental data.

σ values ($R = 0.965$) were obtained. The better correlation with σ^+ values clearly indicates that the propagation, i.e., reaction 4, is predominantly governed by the reactivity of the oxazolinium growing end, e.g., **5** in reaction 4, as discussed above.

Effects of Substituent at the 2 Position of the Oxazoline Ring. It is worthwhile to compare the effects of the substituent at the 2 position on the reactivities because the present study has made the comparison possible on the basis of similar reaction conditions, using MeOTs as initiator in acetonitrile (Table V). With this initiator, polymerizations of the three monomers in Table V proceeded via oxazolinium propagating species. The effects of the substituents H, Me, and Ph are marked. The phenyl substituent decreased both the nucleophilicity (from k_i) and polymerizability (from k_p).

Experimental Section

Materials. Monomers **1a**, **1c**, and **1d** were prepared by the thermal isomerization of *N*-benzoyl-, *N*-(*p*-methoxybenzoyl)-, and *N*-(*p*-chlorobenzoyl)ethylenimine in the presence of NaI:[10] **1a**, bp 53 °C (0.5 mm) [lit.[10a] bp 75.5–78.2 °C (2 mm)]; **1c**, mp 71–72 °C (from $CHCl_3$/diethyl ether). Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.61; H, 6.27; N, 7.77. **1d**, mp 85–86 °C (from $CHCl_3$/diethyl ether) [lit.[10b] 82 °C]. Monomers **1b** and **1e** were obtained by the reactions of *p*-toluonitrile and of *p*-nitrobenzonitrile with 2-aminoethanol in the presence of $ZnCl_2$ catalyst:[11] **1b**, mp 71–72 °C [lit.[12] 67–68 °C]; **1e**, mp 180 °C [lit.[13] mp 180 °C]. All five of these monomers (**1a–e**) showed IR bands of $\nu_{C=N}$ at 1644 cm^{-1} and ν_{COC} at 1260 cm^{-1}. MeOTs and $MeOSO_2CF_3$ were obtained and purified as previously reported.[4,5] CH_3CN and CD_3CN were dried over P_2O_5, distilled, and kept over molecular seives under N_2.

Kinetic Procedures. A typical run of the polymerization kinetics was as follows. Into an NMR sample tube under N_2 at room temperature were placed 2-phenyl-2-oxazoline (**1a**) (0.378 mmol), MeOTs (12 μL = 0.0083 mmol), CD_3CN solvent (0.3 mL), and an internal standard of cyclohexane (5.0 μL). The tube was sealed and shaken well at room temperature. Then, the tube was placed in the NMR probe kept at the reaction temperature, e.g., 100 °C, and the reaction was monitored by recording the NMR spectrum at several times on a Hitachi R-20B NMR (60 MHz) spectrometer. The extent of the reaction before the NMR recording was negligible.

A typical kinetic run of the ring-opening reaction of oxazolinium ion **7** by **1a** (reaction 14) was carried out in the following way. Into an NMR sample tube containing 0.37 mmol of 2-phenyl-2-oxazoline (**1a**) in 0.3 mL of CD_3CN under N_2, 0.37 mmol of $MeOSO_2CF_3$ was added at 0 °C and shaken well. The reaction was complete within several minutes and gave an oxazolinium salt **7**. After 30 min at room temperature, 0.22 mmol of **1a** and cyclohexane (5 μL, an internal standard for integration) were added to the mixture. The tube was sealed, shaken well, and kept at the reaction temperature in the NMR probe insert, and the reaction was monitored by recording the spectrum. A similar procedure was used for reactions of oxazolinium salts of **1b–e** with **1a**.

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	H	p-CH_3	p-OCH_3	p-Cl	p-NO_2
σ	0	−0.170	−0.268	+0.227	+0.778
σ^+	0	−0.311	−0.778	+0.114	+0.790

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