Polymer Journal, Vol. 4, No. 1, pp 87—92 (1973)

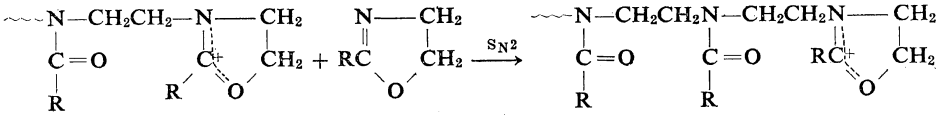
Isomerization Polymerization of 2-Oxazoline. III. Reactivities of Unsubstituted and 2-Substituted 2-Oxazoline Monomers

Takeo SAEGUSA, Hiroharu IKEDA*, and Hiroyasu FUJII**

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

(Received April 10, 1972)

ABSTRACT: In the cationic isomerization polymerization of oxazoline with the initiator of methyl tosylate (MeOTs), the reactivities of 2-oxazoline (OXZ), 2-methyl-2-oxazoline (MeOXZ), and 2-phenyl-2-oxazoline (PhOXZ) were examined. The polymer yield in the same reaction time with the initiator of MeOTs decreased in the order of OXZ > MeOXZ > PhOXZ. The analysis of these relative reactivities was made on the basis of the principle that the rate of polymerization of the S_N2 mechanism is controlled by the concentration of propagating species of oxazolinium, its ring-opening reactivity and the nucleophilic reactivity of monomer.



Equimolar reactions of each monomer with MeOTs were followed by NMR spectrum, and the order of reaction rate was MeOXZ > OXZ > PhOXZ. Then the ring-opening reactivities of oxazolinium ions from three monomers were examined by equimolar reactions of *N*-methyl-oxazolinium tosylates of MeOXZ and PhOXZ with each monomers. The order of reactivity of oxazolinium salt was OXZ > PhOXZ > MeOXZ. From these results of the equimolar reactions, the over-all reactivities of polymerization of three oxazoline monomers were rationalized.

KEY WORDS 2-Oxazoline / 2-Methyl-2-oxazoline / 2-Phenyl-2-oxazoline / Isomerization Polymerization / Ring-opening Reactivities / Methyl Tosylate / Oxazolinium Salt /

In a previous publication[1] we reported the first success in the cationic polymerization of unsubstituted 2-oxazoline (OXZ) to give poly(*N*-formylethylenimine) under milder conditions than those known for 2-substituted-2-oxazolines. The behavior of the propagating species in the OXZ polymerization catalyzed by several cationic initiators was then examined by NMR spectra.[2] The present paper describes the examination of the rate controlling factors of the polymerization initiated by methyl tosylate (MeOTs) which has been shown to proceed through the propagating species of the oxazolinium ion.[2] The relative rates of polymerization of OXZ, 2-methyl-2-oxazoline (MeOXZ), and 2-phenyl-2-oxazoline (PhOXZ) were analyzed on the basis of the results of the equimolar reactions of each monomer with the MeOTs initiator as well as with oxazolinium salts. The kinetic analysis was performed by means of NMR spectroscopy.

EXPERIMENTAL

Reagents

Monomers. OXZ was prepared and purified as before.[1] MeOXZ was prepared by the isomerization reaction of *N*-acetylethylenimine

* Present address: *Tokyo Research Laboratories, Japan Synthetic Rubber Co., Kawasaki, Kanagawa, Japan.*

** Present address: *Research Center, Mitsui Petrochemical Industries, Ltd., Waki-mura, Kuga-gun, Yamaguchi, Japan.*

according to Kagiya[3] and dried with molecular sieves 4A, bp 110°C. PhOXZ was prepared similarly from *N*-benzoylethylenimine[3] and dried by metallic sodium, bp 83°C (1.7 mm).

Catalysts. Commercial reagents of CH_3I and MeOTs were purified by distillation under nitrogen.

Solvents. DMF and acetonitrile were purified by distillation under nitrogen and dried with molecular sieves 4A. Acetonitrile-d_3 (CD_3CN) was the commercial reagent, dried with molecular sieves 4A and distilled under nitrogen.

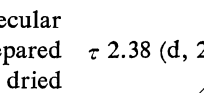
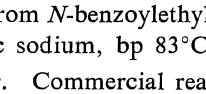
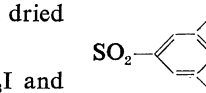
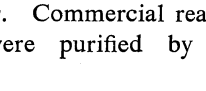
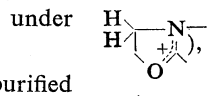
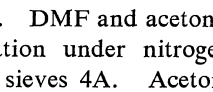
Polymerization

To a mixture of monomer and solvent in a glass ampoule, the initiator was added at 0°C with magnetic stirring. The ampoule was then sealed and stirred at 80°C for 5 hr. In the polymerization of OXZ, the product polymer precipitated as the reaction progressed and the reaction mixture was worked up by the treatment with methanol. In the cases of MeOXZ and PhOXZ the polymerization systems remained homogeneous, and after the polymerization the product polymers were precipitated in diethyl ether, filtered, and dried *in vacuo*.

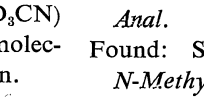
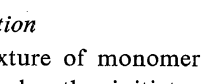
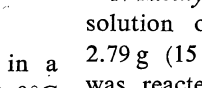
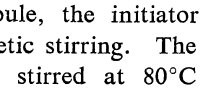
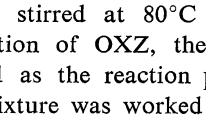
Equimolar Reactions of Monomers with Initiator and with Oxazolinium Salts

The whole operation was carried out in a NMR tube under nitrogen. In the reaction with MeOTs, a desired amount of this initiator was slowly added at −30°C to the stirred monomer solution in CD_3CN. In the case of the oxazolinium salts, the monomer was similarly reacted with these species in CD_3CN at 20°C. After the reaction at a desired temperature, the rection mixture was directly subjected to NMR measurements.

Preparation of Oxazolinium Salts

N-Methyl-2-methyl-2-oxazolinium Tosylate 1. To a solution of 4.19 g (22.5 mmol) of MeOTs in 2 m*l* of ether was added 0.638 g (7.5 mmol) of MeOXZ. The solution was stirred at 30°C for 2 hr to produce a white precipitate. Then 20 m*l* of ether was added to the mixture and the precipitated salt was isolated from the acetonitrile—ether system to give 1.34 g (66%) of white crystal: IR (Nujol) 1685 (C=N—), 1283 (C—O—C), and 981 cm^{-1} (skeletal). NMR (CD_2CN) τ 2.38 (d, 2, ), 2.82 (d, 2, ), 5.20 (t, 2, ), 5.94 (t, 2, ), 6.80 (s, 3, $\overset{+}{N}$—CH_3), 7.70 (s, 3, ), and 7.72 ppm (s, 3, ).

Anal. Calcd for $C_{12}H_{17}NO_4S$: S, 11.82. Found: S, 11.48.

N-Methyl-2-phenyl-2-oxazolinium Tosylate 2. A solution of 1.1 g (7.5 mmol) of PhOXZ and 2.79 g (15 mmol) of MeOTs in 2 m*l* of ether was reacted at 80°C for 2 hr in a sealed tube. To the reaction mixture 20 m*l* of ether was added to give a highly viscous product, which was repeatedly reprecipitated by the acetonitrile—ether system. The yield was 1.87 g (75%): IR (neat) 1665 (C=N—), 1290 (C—O—C), and 913 cm^{-1} (skeletal); NMR (CD_3CN) τ 2.10—2.80 (complexed m, 7, ), 2.88 (d, 2, ), 4.93 (t, 2, ), 5.53 (t, 2, ), 6.60 (s, 3, $\overset{+}{N}$—CH_3), and 7.71 ppm (s, 3, ). *Anal.* Calcd for $C_{17}H_{19}NO_4S$: S, 9.62. Found: S, 9.06.

NMR Spectra

NMR spectra were taken on a Varian HA-100 instrument using TMS as the internal standard.

RESULTS AND DISCUSSION

Polymerization of Oxazolines

The results of the polymerizations of three oxazoline monomers by several initiators in DMF at 80°C are shown in Table I. The table shows that OXZ was the most reactive and that the reactivities of these monomers in the polymerization followed the order of OXZ > MeOXZ > PhOXZ, except for the case of the CH_3I initiator. The different result with the CH_3I initiator is rationalized by the fact that

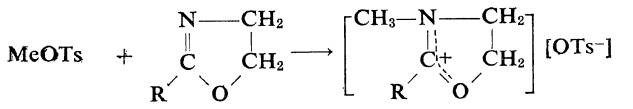
Table I. Polymerization of 2-oxazolines[a]

Initiator	Conversion, %		
	OXZ	MeOXZ	PhOXZ
MeOTs	91	61	trace
BF_3OEt_2	75	48	8
CH_3I	29	95	8

[a] Monomer, 3.0 mol/*l*; initiator, 0.03 mol/*l*; solvent, dimethylformamide 4 m*l*; 80°C, 5 hr.

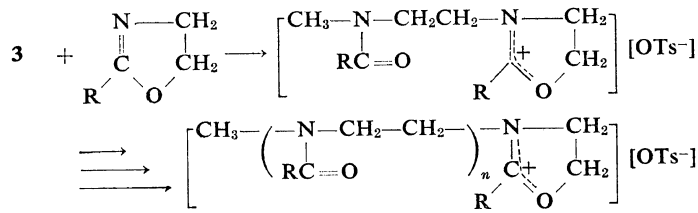
the polymerization of OXZ by CH_3I proceeds through a different propagating species of the ring-opened iodide owing to the high ring-opening ability of OXZ monomer.[2] On the other hand, the polymerizations of the other two monomers by the same initiator proceeded through the propagating species of the corresponding oxazolinium iodides.[2]

As already established,[2] the OXZ polymerization by the MeOTs initiator proceeds *via* the following mechanistic scheme, which consists of the two elementary processes of eq 1 and 2.



(1)

3



(2)

In the first process (eq 1), an oxazolinium salt **3** is produced by the reaction of the initiator with monomer. The rate of this reaction will depend on the nucleophilic reactivity of the monomer, the rate of this reaction controlling the concentration of the propagating species of oxazolinium in the polymerization. The second reaction is the so-called propagation, which is the ring-opening of the oxazolinium ion at the growing chain end by the nucleophilic attack of the oxazoline monomer. The reaction rate of the propagation is governed by three factors, the concentration of the propagating species, the ring-opening reactivity of the growing oxazolinium ion, and the nucleophilic reactivity of the monomer. The kinetics of the oxazoline polymerization are to be analyzed from these two elementary processes, for which the equimolar reactions of monomers with a catalyst as well as with the isolated oxazolinium ion salts are to be examined separately.

Equimolar Reactions

Initiation Reaction (*The Equimolar Reaction of the MeOTs Initiator with Oxazoline*). Equimolar amounts of MeOTs and a oxazoline monomer were reacted in acetonitrile-d_3 in an NMR tube at 60°C. The reaction mixture in a tube was subjected to inspection by NMR spectroscopy at a desired time of reaction by the method shown in our previous study.[2] A typical example of the NMR spectrum of the reaction between MeOTs and MeOXZ is given in Figure 1.

The percent conversion of the initiator can be calculated from the area ratio of the peaks at τ 2.82 (reacted MeOTs) and τ 2.60 (unreacted MeOTs). The percent conversion of monomer can also be calculated from the peak areas of methyl protons of the reacted monomer (τ 7.71 and τ 8.02) and unreacted monomer (τ 8.10). Because the methyl protons of the propagating oxazolinium cation and the tosylate counter-anion overlap each other at τ 7.71, as is indicated in the spectrum of the 1 : 1 salt of MeOXZ and MeOTs (see EXPERIMENTAL), the half value of the total peak area was conveniently adopted as that of the reacted monomer. Thus, the conversions of the

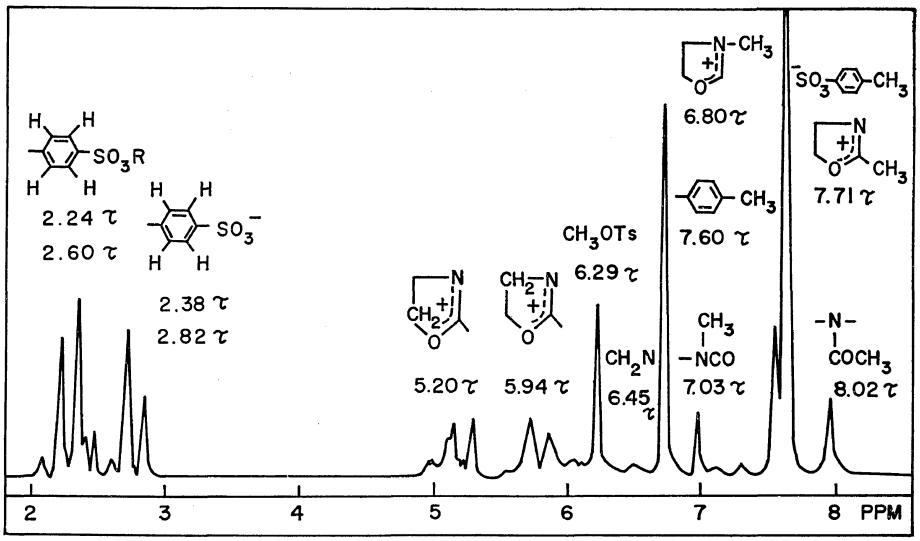


Figure 1. NMR spectrum of reaction mixture of equimolar reaction of MeOXZ with MeOTs in CD_3CN at 60°C for 10 min.

monomer and the initiator in Figure 1 were calculated at 100 and 72%, respectively. In this system, the peak at τ 6.80 is assigned to $\overset{+}{N}$—CH_3 of oxazolinium ion as is shown in the spectrum of the MeOXZ salt of MeOTs and the one at τ 7.03 is due to N—CH_3 at the ends of the higher oligomeric species produced in eq 2. The sum of *N*-methyl protons at τ 6.80 and τ 7.03 agreed well with the amount of the reacted MeOTs (τ 2.82). The peak at τ 5.20 and τ 5.94 could be assigned to the *O*-methylene protons of the oxazolinium salt, respectively, whose amount coincided with that of the initiator reacted.

From these results it is clear that the equimolar reaction of MeOTs with MeOXZ initially produces *N*-methyl-2-methyl-2-oxazolinium tosylate **1** which is then successively reacted with monomer to give oligomer having oxazolinium salt at the growing chain end. In the same manner the reaction of PhOXZ with MeOTs was examined. The results are summarized in Table II together with the reactions of OXZ[2] and MeOXZ with MeOTs. After 10 min at 60°C OXZ and MeOXZ were consumed quantitatively, whereas the conversion of PhOXZ was only 19%. The values of the conversion percent of initiator in the reactions

Table II. Equimolar reaction of 2-oxazolines with MeOTs[a]

Monomer	Reaction		Conversion, %	
	Temp, °C	Time, min	MeOTs	Monomer
OXZ	60	10	26	100
MeOXZ	60	10	72	100
PhOXZ	60	10	19	19
OXZ	35	30	15	40
MeOXZ	35	30	34	41

[a] Monomer, 3.8 mmol; MeOTs, 3.8 mmol; solvent, CD_3CN; CD_3CN/monomer=4 (vol/vol).

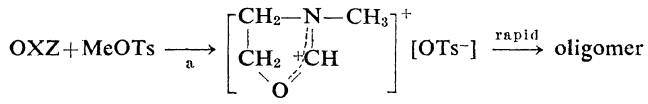
with OXZ and with MeOXZ at 60°C are taken to suggest that the rate of the MeOTs—monomer reaction is higher with MeOXZ than with OXZ. The higher reactivity of MeOXZ towards MeOTs in comparison with OXZ was shown clearly in a separate series of experiments carried out at 35°C (Table II). Evidently a larger amount of MeOTs was consumed by the reaction with MeOXZ (34%) than with OXZ (15%) after 30 min where the conversions of the two monomers were similar to each other.

From the above results, the following order of reactivity in initiation is given: MeOXZ > OXZ > PhOXZ. This order may be generally

regarded as the relative S_N2 nucleophilic reactivities of three monomers. Here it is important to note that this order of nucleophilic reactivity does not coincide with the order of polymerization reactivity.

Propagation Reaction (Equimolar Reaction of Oxazolinium Salt with Monomer). As has been mentioned before, the rate of propagation is controlled by the ring-opening reactivity of oxazolinium salt at the propagating end and by the nucleophilic reactivity of the monomer. For the analyses of the reactivities of the species concerned, equimolar reactions of the isolated oxazolinium salts with monomers were examined.

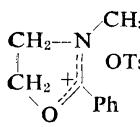
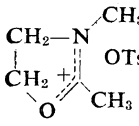
Tosylate salts of *N*-methylMeOXZ (**1**) and *N*-methyl-PhOXZ (**2**) were prepared by the reactions of the corresponding monomers with excess of MeOTs in diethyl ether. In the case of OXZ, however, only oligomeric oxazolinium salt was abtained and the corresponding *N*-methyloxazolinium tosylate could not be isolated.



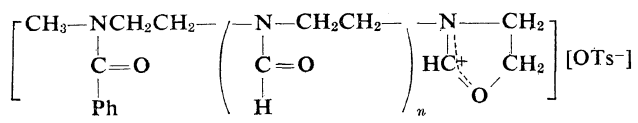
Each of the two oxazolinium tosylates of **1** and **2** was subjected to the reaction with one of three monomers. The results are given in Table III. In the first series of reactions, the consumption percents of **2** in its reactions with three oxazoline monomers are taken to show the relative nucleophilic reactivity of monomer. The order, MeOXZ>OXZ>PhOXZ, is in good qualitative agreement with the order given in the reaction of MeOTs with these monomers (*cf.* Table II). Furthermore, it is important that the percent conversion of monomers is in the order of OXZ>MeOXZ>PhOXZ. This order is reasonably rationalized by assuming that the oxazolinium salt of OXZ **4** derived from **2** and OXZ is much more reactive in comparison with the corresponding oxazolinium salts of MeOXZ and PhOXZ.

In the second series, **1** was reacted with MeOXZ and with PhOXZ. The conversion percent of **2** in the reaction with MeOXZ is higher than that of **1** in the reaction with the same monomer. Qualitatively, this comparison means that **2** is more reactive than **1**. Thus the following order of the ring-opening reactivities of oxazolinium salts is given.

Table III. Equimolar reaction of 2-oxazolines with 2-oxazolinium tosylates[a]

Oxazolinium salts	Monomer	Conversion, %	
		Oxazolinium salt	Monomer
 **2**	OXZ	26	100
	MeOXZ	59	63
	PhOXZ	0	0
 **1**	MeOXZ	23	38
	PhOXZ	0	0

[a] Oxazolinium salt, 1—2 mmol; monomer/salt=1 (mol/mol); solvent(CD_3CN)/monomer=4 (vol/vol); at 60°C, for 10 min.

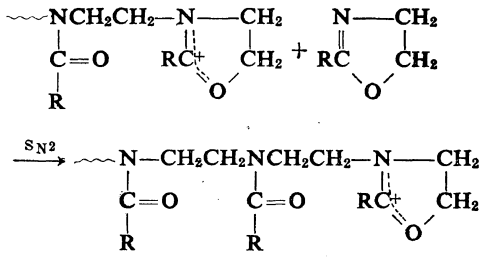


4

(n=0, 1, 2, . . .)

Oxazolinium salt of OXZ>
that of PhOXZ>that of MeOXZ

The oxazoline polymerization is expressed by the scheme,



The rate equation is[4]

$$-\frac{d[M]}{dt}=k_p[P^*][M]$$

where k_p is the rate constant of the propagation reaction, [P*] is the concentration of the propagating species, and [M] is the instantaneous monomer concentration. The propagating species of oxazolinium salt is formed in the reaction of the initiator with monomer and so [P*] is governed by the nucleophilic reactivity of the monomer toward the initiator. In this study, the reactivity in the initiation reaction by MeOTs was shown to decrease in the following order: MeOXZ>OXZ>PhOXZ. So, [P*] values may reasonably be assumed to be in the same order.

On the other hand, k_p is considered to be controlled by the ring-opening reactivity of the oxazolinium growing end and the nucleophilic reactivity of the monomer. The ring-opening reactivities of the oxazolinium growing ends were assumed to be in the order of OXZ> PhoXZ>MeOXZ. The combination of these three factors, [P*], the ring-opening reactivity of the oxazolinium growing end, and the nucleophilic reactivity of monomer, may lead to the following observed order of the polymerization rate, OXZ> MeOXZ>PhOXZ. In other words, the high overall reactivity of polymerization of OXZ is due to the high ring-opening reactivity of the oxazolinium growing end.

The present study has demonstrated an important concept that the so-called overall reactivity of polymerization of oxazoline monomer is controlled by three factors. A series of quantitative kinetic analyses of the polymerizations of some oxazoline monomers are being carried out now, and the results will be published in the near future.

REFERENCES

1. T. Saegusa, H. Ikeda, and H. Fujii, *Polymer J.*, **3**, 35 (1972).
2. T. Saegusa, H. Ikeda, and H. Fujii, *ibid.*, **3**, 176 (1972).
3. T. Kagiya, S. Narisawa, T. Maeda, and K. Fukui, *Kogyo Kagaku Zasshi* (*J. Chem. Soc., Japan, Chem. Ind. Sect.*), **69**, 732 (1966).
4. A. Tomalia and D. P. Sheetz, *J. Polym. Sci., Part A-1*, **4**, 2253 (1966).