# POLYMERIZATION AND COPOLYMERIZATION OF CYCLIC IMINO-ETHERS

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Polymerizations of the cyclic imino-ethers, 2-oxazoline and 5,6-dihydro-4*H*-1,3-oxazine are recorded. Homopolymers of these two compounds poly(*N*-formylethylenimine) and poly(*N*-formyltrimethylenimine), were readily hydrolysed by alkali to produce crystalline polymers of polyethylenimine and poly(trimethylenimine), respectively. Kinetic analysis was made of the polymerizations of these monomers. The difference in polymerization reactivity between them was discussed. Finally, a novel type of spontaneous 1:1 alternating copolymerization of cyclic imino-ethers with other functional monomers was described. For this type of reaction, a new concept of alternating copolymerization has been presented, involving betaine as a key intermediate.

Many studies have been made of the polymerizations of the five- and six-membered cyclic imino-ethers, **1** and **2**, substituted at the 2-position[1-9]. The ring-opening propagation involves isomerization, and the resulting polymers are poly(*N*-acylalkylenimines), **3** and **4**. Unsubstituted imino-ethers (R = H in **1** and **2**), however, have not yet been polymerized.
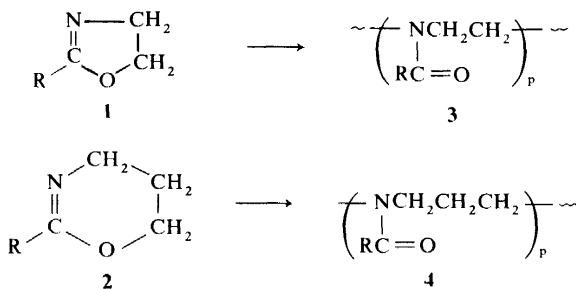
Recently, we have succeeded in the polymerizations of unsubstituted 2-oxazoline (OZO) (**1**, R = H)[10, 11] and unsubstituted 5,6-dihydro-4*H*-1,3-oxazine (OZI) (**2**, R = H)[12]. The polymer products, poly(*N*-formylethylenimine) (**3**, R = H) and poly(*N*-formyltrimethylenimine) (**4**, R = H), were readily hydrolysed to produce poly(ethylenimine)[10, 11] and poly(trimethylenimine)[12], respectively. Polyalkylenimines thus prepared have been shown to be crystalline. So far as we know, it is the first time crystalline polyethylenimine and poly(trimethylenimine) have been prepared.

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By using these two monomers, OZO and OZI, we have explored some new fields in ring-opening polymerization[6-15].

In the present article, the following three topics are described and discussed.

(1) Cationic polymerizations of OZO and OZI, and the hydrolyses of the polymers to poly(ethylenimine)[10,11] and poly(trimethylenimine)[12], respectively.

(2) Kinetics of the polymerizations of OZO and OZI with methyl tosylate (MeOTs)[13,14] as initiatior. The polymerization reactivities of these two monomers differing in ring size are compared with each other.
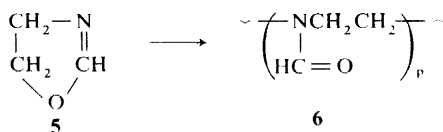
(3) Spontaneous alternating copolymerization of cyclic imino-ethers with other functional monomers[15,16].

1. CATIONIC POLYMERIZATION OF OZO AND OZI, AND THE HYDROLYSES OF POLYMERS
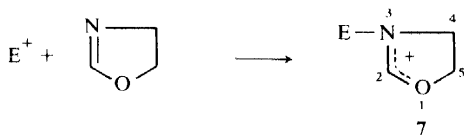
1.1 Polymerization of OZO[10]

As mentioned before, polymerizations of several substituted oxazolines have been reported before our study[1-9]. But, unsubstituted 2-oxazoline has not been polymerized yet. Thermodynamic studies of the ring-opening polymerization have disclosed that the unsubstituted cyclic monomer has a higher thermodynamic polymerizability compared with the substituted ones[20,21]. According to this general tendency, OZO was deemed polymerizable.

In our study, OZO was synthesized according to a literature procedure[22], and was found to contain a considerable amount of water. Its purification was readily accomplished by treatment with Molecular Sieves 4A. Then, the purified OZO monomer was successfully polymerized by several cationic initiators, such as metal fluorides, sulphate ester, sulphonate esters, sulphuric acid, and alkyl iodide[10]. As the reaction solvent, aprotic polar solvents such as DMF, CH_3CN, and nitrobenzene were suitable.

$$CH_2-N \atop CH_2 \quad CH \atop \diagdown O \diagup \quad \longrightarrow \quad \left(\begin{matrix} -NCH_2CH_2- \\ | \\ HC=O \end{matrix} \right)_p$$

$$5 \qquad\qquad\qquad\qquad 6$$

The resulting polymer was water-soluble and crystalline, melting at about 210 °C. Its structure, as poly(N-formylethylenimine) 6, was established by n.m.r. and i.r. spectroscopy as well as by elemental analysis. *Figure 1* shows the n.m.r. spectrum of the polymer in deuterium oxide. The simple spectrum consisting of two singlets at τ 2.02 ($-C\underline{H}O$, 1H) and at τ 6.45 ($>NC\underline{H}_2C\underline{H}_2-$, 4H) shows a clean structure of the polymer. A peak at τ 5.2 is due to water contained in the deuterium oxide.

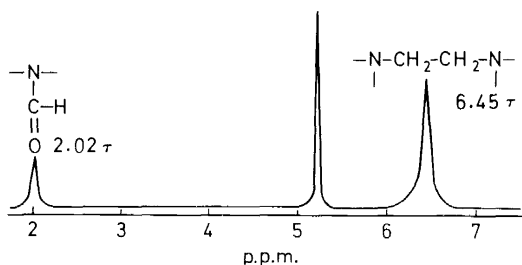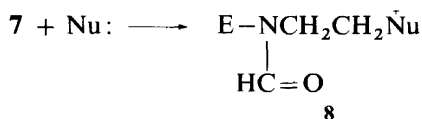The isomerization polymerization of OZO is formulated as follows:

$$E^+ + \left[\begin{matrix} N \\ \diagdown O \end{matrix} \right] \quad \longrightarrow \quad \left[\begin{matrix} E-N \\ {}_2\diagdown O \diagup {}^5 \\ | \\ 1 \end{matrix} \right]^+$$

$$7$$

$$7 + Nu: \longrightarrow E-NCH_2CH_2\overset{+}{N}u$$

$$\underset{\underset{\textbf{8}}{HC=O}}{|}$$

Figure 1. N.m.r. spectrum of poly-OZO in D_2O.

The monomer reacts with electrophile E^+ to form oxazolinium ion **7**, which is then opened with isomerization by the attack of a nucleophile at the 5-methylene group. Except for the polymerization by methyl iodide, the OZO monomer functions as a nucleophile to produce oxazolinium ion successively in propagation[13]. Repetition of the isomerization ring-opening gives rise to structure **6**.

1.2 Hydrolysis of poly(OZO)

$$6 \xrightarrow[\text{OH}^-]{\text{H}_2\text{O}} \sim \underset{\textbf{9}}{+NHCH_2CH_2+_p} \sim$$
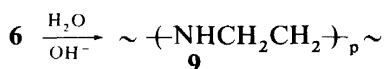
Poly(OZO) **6** was readily hydrolysed in water by alkali to polyethylen-imine. The extent of hydrolysis reaction was proportional to the amount of alkali. *Figure 2* shows that the *N*-formyl group is hydrolysed proportion-
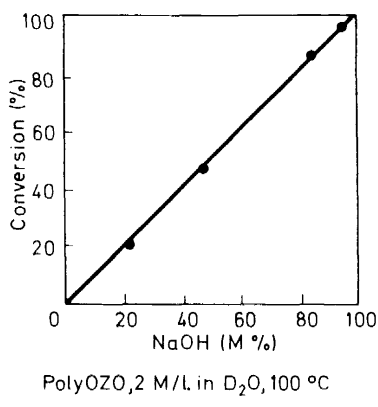

PolyOZO, 2 M/l. in D_2O, 100 °C

3h

Figure 2. Alkaline hydrolysis of poly-OZO (Poly-OZO 2 mole/1 in D_2O, 100 °C, 3 h).

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ately to the alkali consumed. Thus, the composition of the partly hydrolysed poly(OZO) is easily controlled by the amount of alkali. In the partly hydrolysed poly(OZO), the mode of distribution of the N-formylethylenimine unit and the ethylenimine unit is a future problem of interest.

Complete hydrolysis gave polyethylenimine, which was found to be soluble in hot water but insoluble in cold water. It could be purified by recrystallization from water. *Figure 3* shows the n.m.r. spectrum of poly-
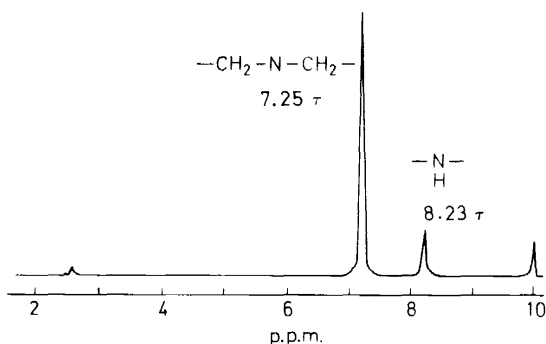

Figure 3. N.m.r. spectrum of polyethylenimine in CDCl$_3$.

ethylenimine in deuteriochloroform, in which only two singlets, τ 7.30 (4H) and τ 8.43 (1H), are seen. The latter peak almost disappeared on treatment with deuterium oxide. The elemental analysis of the completely hydrolysed poly(OZO) agreed with the calculated value for polyethylenimine.

The polymer from 2-methyl-2-oxazoline has the structure of poly(N-acetylethylenimine). The literature[4] described that poly(N-acetylethylenimine) was not completely hydrolysed by alkali.

Polyethylenimine, prepared from poly(OZO), is crystalline. According to the conditions of drying of the sample prepared by recrystallization from water, the content of water of crystallization varied. In our preliminary experiments, two crystalline forms of poly(ethylenimine) have been prepared. Their x-ray patterns are shown in *Figure 4*. The one is anhydrous, melting at 58.5 °C, which was prepared by drying in a vacuum at temperatures above 60 °C. The other is a hydrated form, melting at 78.5 °C, containing about 15 mole% of water of crystallization, which was prepared by drying in a vacuum at temperatures below 50 °C.

Poly(ethylenimine), prepared from poly(OZO), is crystalline and insoluble in cold water. It is quite stable in air. These properties are strikingly different from those of the conventional poly(ethylenimine) produced by the cationic polymerization of ethylenimine. The conventional one is amorphous and readily soluble in cold water, and it is prone to oxidation in air. The difference of the properties is ascribed to the difference of molecular structure. Poly(ethylenimine) from poly(OZO) has a linear structure without branching, whereas the conventional one has a highly branched structure. According to Dick and Ham[23], the branching in the conventional one is distributed randomly at an average ratio of one branch per 3.0 to 3.5 units.
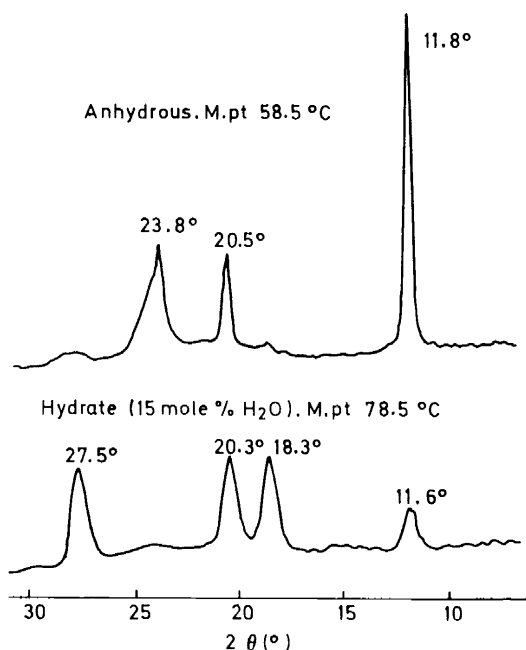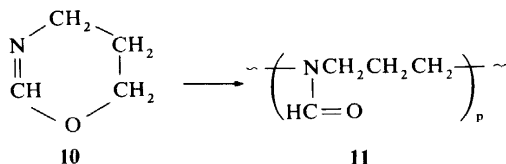
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Figure 4. X-ray spectra of polyethylenimine. (Anhydrous and hydrated samples.)

1.3 Polymerization of OZI[1 2]

Before our study, compound **10** was not known. The preparative method for the 2-substituted compounds was not applicable to the synthesis of the unsubstituted compound **10**. Coincidentally a general synthesis of cyclic imino-ethers has recently been developed by us[24]; this is accomplished by the reaction of amino-alcohol with isonitrile in the presence of silver cyanide. By means of our new synthetic method, compound **10** was prepared successfully by the reaction of 3-aminopropanol with t-butyl isocyanide in the presence of silver cyanide[12]:

$$HO(CH_2)_3NH_2 + t\text{-}BuNC \xrightarrow[\text{b.p. 54-56 °C/56 mmHg}]{\text{AgCN}} 10 + t\text{-}BuNH_2$$
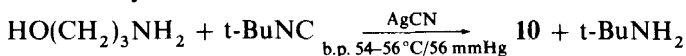
OZI thus synthesized was polymerized by cationic initiators such as sulphate, sulphonate, methyl iodide, and boron trifluoride. The product was poly-(N-formyltrimethylenimine) **11**, which was a partly crystalline solid melting

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at 120–125 °C. The structure of **11** was established by n.m.r. and i.r. spectra. In its n.m.r. spectrum (*Figure 5*) there are a singlet at τ 1.86 (formyl proton, 1H), a triplet-like broad signal centred at τ 6.56 (*N*-methylene protons, 4H) and a broad signal centred at τ 1.06 (*C*-methylene protons, 2H). The i.r. spectrum was quite compatible with the structure **11**.
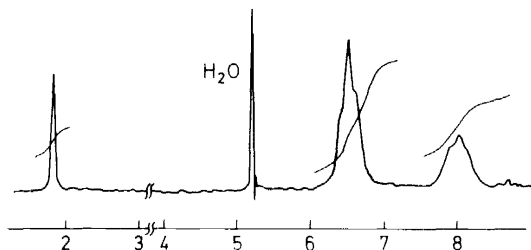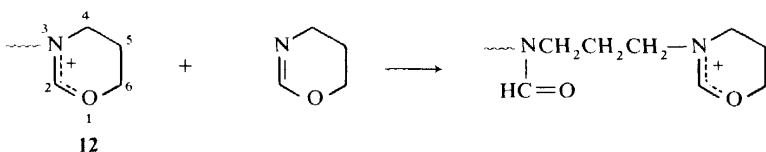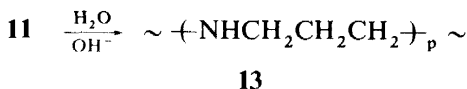

Figure 5. N.m.r. spectrum of poly-OZI in D_2O.

The course of the isomerization propagation of **10** is formulated as follows:

The cyclic oxonium-ammonium species at the propagating end **12** is opened with isomerization by the nucleophilic attack of monomer on to the 6-position of **12**.

1.4 Hydrolysis of poly(OZI)[12]

$$\mathbf{11} \quad \xrightarrow[\text{OH}^-]{\text{H}_2\text{O}} \quad \sim \text{--}(\text{NHCH}_2\text{CH}_2\text{CH}_2\text{)}_p \sim$$

13

The OZI-polymer **11** was readily hydrolysed by alkali in a 1/1 methanol-water mixture to produce poly(trimethylenimine) **13**. The structure of **13** was confirmed by n.m.r. and i.r. spectra. *Figure 6* shows the n.m.r. spectrum, which consists of a broad singlet at τ 7.27 (*N*-proton, 1H), a triplet centred at τ 7.93 (*N*-methylene protons, 4H), a broad multiplet centred at τ 8.80 (*C*-methylene protons, 2H), and a sharp singlet at τ 5.20 (due to water of crystallization contained in the sample).

So far as we know it is the first time linear poly(trimethylenimine) has been prepared. Poly(trimethylenimine) is partly crystalline and very hygroscopic. Its melting point depends on the content of water of crystallization, e.g. 74–76 °C for a sample containing 9.3 wt % of water and 81–84 °C for one containing 17 wt % of water.
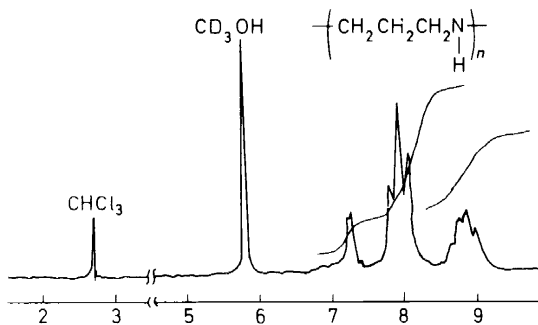
Figure 6. N.m.r. spectrum of polytrimethylenimine in CD_3OD.

2. POLYMERIZATION KINETICS

Kinetic analyses of the polymerizations of OZO^{13} and OZI^{14} by methyl tosylate were performed by use of n.m.r. spectroscopy. The effect of the monomer ring size on polymerization reactivity was examined.

2.1 Polymerization of OZO

Figure 7 shows the n.m.r. spectrum of the system of OZO polymerization by methyl tosylate in trideuterioacetonitrile at 31 °C after 109 min, where
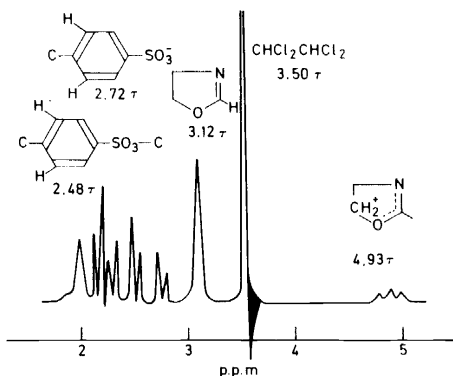

Figure 7. N.m.r. spectrum of the system of the OZO polymerization by MeOTs in CD_3CN (OZO 4.94 mmol, MeOTs 0.988 mmol, CD_3CN 0.84 ml, $Cl_2CHCHCl_2$ 0.5 ml, at 31 °C after 109 min).

the molar ratio of MeOTs/OZO is 1/5. The peak at τ 4.93 is due to the 5-methylene protons of the oxazolinium propagating species, the singlet at τ 3.12 is assigned to the 2-methine proton of the monomer, and the peaks at τ 2.72 and 2.48 are assigned, respectively, to the benzene-ring hydrogens of tosylate counter-anion and tosylate ester. Instantaneous concentrations of three species, i.e. monomer, initiator, and propagating species, were deter-
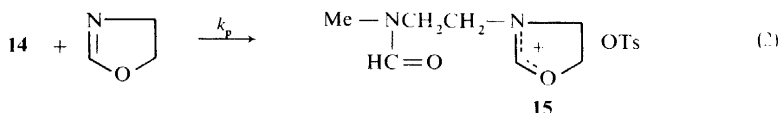
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mined. Then, the variations of these concentrations with the reaction time were known.

The scheme of this polymerization is formulated as follows:

Initiation:

(1)

Propagation:

(2)

Generally,

(3)
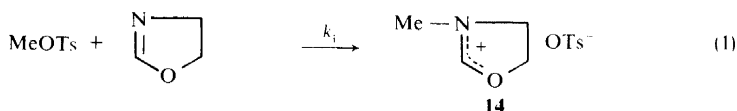
Initiation [equation (1)] is the reaction of OZO with MeOTs to produce the first propagating species, **14**. Propagation [equations (2) and (3)] is the S_N2 reaction between the propagating species, oxazolinium tosylate (**14** and **16**) and OZO.

The following rate equations are constructed:

Initiation:

$$- d[I]/dt = k_i[I][M]$$

where $[I]$ and $[M]$ are the concentrations of MeOTs and OZO, respectively. Integration gives,

$$\ln ([I]_0/[I]_t = k_i \int_0^t [M]\,dt \tag{4}$$

Propagation:

$$- d[M]/dt = k_i[I][M] + k_p[P^*][M]$$

where $[P^*]$ is the concentration of propagating species. Since the relationship, $[P^*] = [I]_0 - [I]$, has been established by n.m.r. spectrosopy.

$$- d[M]/dt = (k_i - k_p)[I][M] + k_p[I]_0[M]$$

Integration gives,

$$\frac{\ln [M]_0/[M]_t}{\int_0^t[I]dt} = (k_i - k_p) + k_p \frac{[I]_0 t}{\int_0^t[I]dt} \tag{5}$$

Kinetic analysis on both initiation and propagation was made according to the integrated rate equations, equations (4) and (5). The integrated values of concentrations of monomer in equation (4) and of initiator in equation (5)

were given by graphical integration on the $[M] \sim$ time and $[I] \sim$ time curves, respectively. Each plot of equations (4) and (5) was a straight line, whose slope corresponds to the respective rate constant (*Table 1*). From the temperature change of k_p, the activation parameters were calculated (*Table 1*).

Table 1. Kinetic data by polymerizations of OZO and OZI by MeOTs in CD_3CN

Rate constants ($\times$ 10^{-4} 1^{-1} mol s^{-1})			
OZO		OZI	
k_i	k_p	k_i	k_p
0.14 (24 °C)	1.9 (24 °C)		0.44 (40 °C)[a]
0.29 (31 °C)	4.6 (31 °C)	9.0 (35 °C)	0.8 (45 °C)
0.98 (40 °C)	19 (40 °C)	11.8 (40 °C)	1.6 (53 °C)
		14.8 (45 °C)	3.4 (60 °C)
		18.2 (51 °C)	8.6 (71 °C)

Activation parameters of propagation		
	OZO	OZI
E_a (kcal mol^{-1})	25	20
A (l mol^{-1} s^{-1})	7.5×10^{14}	3.6×10^9

[a] Calculated values based on activation parameters.

2.2 Polymerization of OZI

Figure 8 shows an example of a n.m.r. spectrum of the system of the OZI polymerization by methyl tosylate in trideuterioacetonitrile at 53 °C

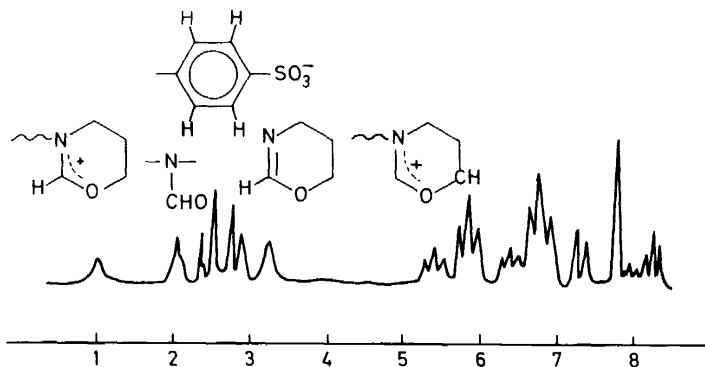*Figure 8*. N.m.r. spectrum of the system of the OZI polymerization by MeOTs in CD_3CN (OZI 1.67 mmol, MeOTs 0.40 mmol in 1.0 ml of CD_3CN solution, at 53°C after 100 min).

after 100 min. The feed ratio of MeOTs/OZI was 1/5. Methyl tosylate had been quantitatively converted into the propagating species of cyclic oxazinium 17. The concentration of propagating species was given separately from a singlet at τ 1.38
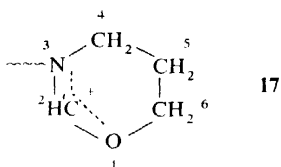
(2-methine hydrogen of **17**, 1H), an A_2B_2 type quartet at τ 2.61 (aromatic hydrogens of tosylate anion, 4H), and a triplet at τ 5.47 (6-methylene hydrogens of **17**, 2H). Stoichiometries (areas of these peaks) were satisfactory, and the concentration of propagating species was equal to the initial concentration of MeOTs. In *Figure 8*, the concentration of monomer was determined by the peak area at τ 3.07. Kinetic analysis of initiation by n.m.r. spectroscopy was made with the system of an equimolar feed, because the rate of consumption of methyl tosylate was rapid.

The reaction scheme and the rate equation are similar to those for OZO polymerization. Kinetic analysis was carried out according to the same procedure. The data are summarized in *Table 1*.

2.3 Comparison of reactivities of OZO and OZI

Table 1 gives k_i, k_p, and the activation parameters of propagation for the polymerizations of OZO and OZI. Comparison of k_i indicates that OZI has a higher nucleophilic reactivity than OZO. As to propagation, k_p of OZO is about 40 times higher than that of OZI. That is, the five-membered monomer is more reactive than the six-membered one. It is more interesting to notice that the higher k_p value of OZO is due to the higher value of the frequency factor, i.e. the entropy factor. The activation energy of the OZO propagation is higher than that of the OZI propagation.

One possible explanation for the activation parameters may be made in terms of the solvation–desolvation phenomena in the course from initial state to transition state. In the initial state, the oxonium-ammonium ring of the propagating species may be highly solvated. In the transition state, the positive charge is distributed over the oxonium-ammonium and the nitrogen atom of the attacking monomer, and hence, the activated complex becomes less solvated. The increase of freedom of the system due to desolvation at the transition state is a factor of the entropy increase. In the initial state, the five-membered oxazolinium ring has a planar structure, and is more solvated than the six-membered oxazinium ring which has a twisted structure. In the oxazinium ring, the 5-methylene group flips above and below the ring plane and impedes solvation (*Figure 9*). Therefore, the activation entropy of the
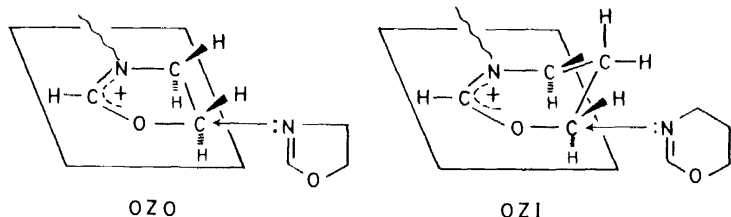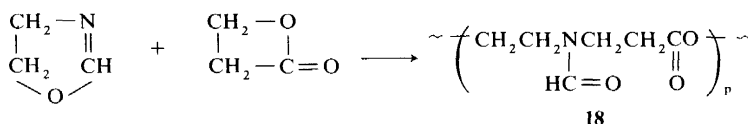

OZO   OZI

Figure 9. Models of propagation in the polymerizations of OZO and OZI.

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OZO propagation is less negative because of the higher entropy gain afforded by the desolvation compared with the OZI propagation. Instead of the favourable frequency (entropy) factor, the OZO propagation requires a higher activation energy for desolvation.

3. SPONTANEOUS ALTERNATING COPOLYMERIZATION OF CYCLIC IMINO-ETHERS WITH OTHER FUNCTIONAL MONOMERS

3.1 Copolymerization of OZO with β-propiolactone (BPL)[15]

When an equimolar mixture of OZO and BPL was placed in an aprotic polar solvent, like DMF, at temperatures as low as 40°C, an exothermic reaction took place, without added initiator, to produce the 1:1 alternating copolymer **18** in high yields.

$$\begin{array}{c} CH_2-N \\ | \quad\quad \| \\ CH_2 \quad CH \\ \diagdown O \diagup \end{array} \quad + \quad \begin{array}{c} CH_2-O \\ | \quad\quad | \\ CH_2-C=O \end{array} \quad \longrightarrow \quad \sim \left(CH_2CH_2NCH_2CH_2CO \right)_n \sim \\ \begin{array}{cc} | & \| \\ HC=O & O \end{array}$$

18

The formation of real copolymer was confirmed by fractionation with solvents. The structure of **18** was established by n.m.r. and i.r. spectra and elemental analysis as well as by analysis of the product of alkaline hydrolysis. By n.m.r. spectroscopy, the products of alkaline hydrolysis of the resulting polymer were shown to be almost exclusively the sodium salts of the acid **19** and of formic acid.
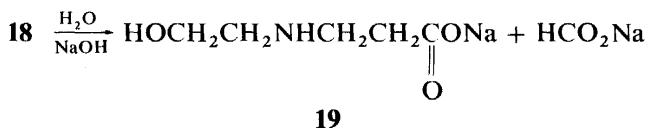
$$\textbf{18} \quad \xrightarrow[\text{NaOH}]{H_2O} \quad HOCH_2CH_2NHCH_2CH_2\underset{\underset{O}{\|}}{C}ONa \quad + \quad HCO_2Na$$

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Figure 10 shows a copolymer composition curve at 40°C in DMF. The apparent values of monomer reactivity ratio are $r_{BPL} = 0.15$ and $r_{OZO} = 0.0$. These values are indicative of the high alternating tendency. It is seen that the 1:1 alternating copolymer is produced when the fraction of OZO in the monomer mixture is above 0.5.

The effect of solvent on the copolymerization is seen in *Table 2*. Aprotic polar solvents, such as DMF and acetonitrile, are preferable. In non-polar solvents like toluene, the yield of copolymer is small. The copolymer composition, however, is not affected by the mature of solvent. The solvent effect is important in the consideration of the mechanism of the alternating copolymerization.

Figure 11 shows a plot of the percent conversion against the molecular weight of the copolymer produced. Three points at higher conversions fall on the straight line passing the origin. Two points at lower conversions deviate above the line. The deviation is due to the fact that the number of copolymer molecules is smaller at lower conversions than that at higher
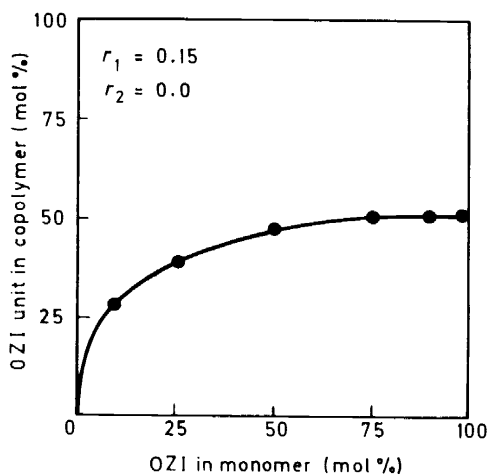
Figure 10. Copolymer composition curve of the OZO–BPL copolymerization.

Table 2. Effect of solvent on the copolymerization of OZO
with BPL[a, 15]

Solvent	Yield of copolymer	OZO in copolymer (mole %)
DMF	70	47
CH_3CN	39	52
$ClCH_2CH_2Cl$	26	50
Bu_2^nO	29	45
Toluene	9	46

[a] $OZO = PBL = 3.75$ mmol; solvent, 2 ml; 40 C, 3 h.
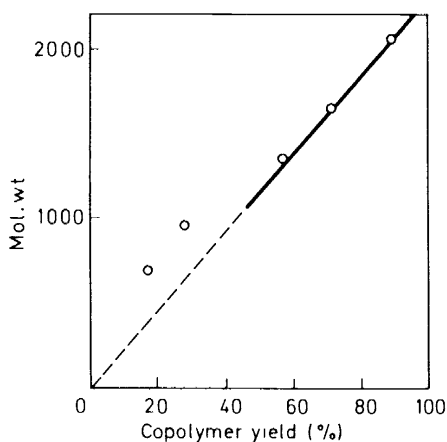
Figure 11. OZO-BPL copolymerization. Percent conversion versus molecular weight of product copolymer.

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conversions. At any rate, this plot shows the absence of chain-transfer reaction during the copolymerization. Together with other observations, the copolymerization has been assumed to proceed through a living polymerization mechanism.

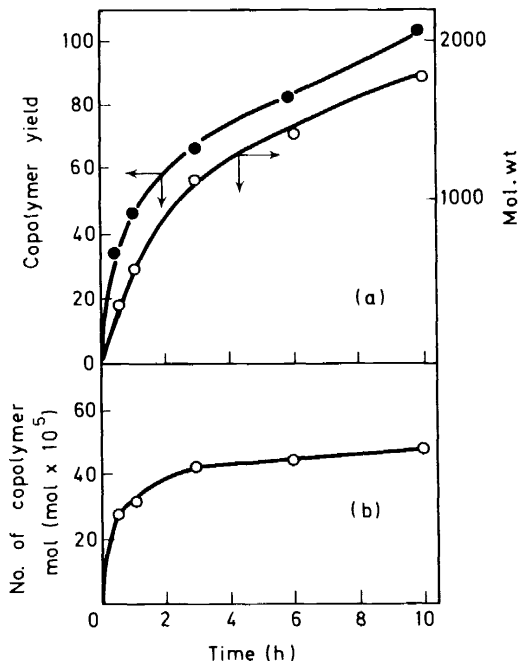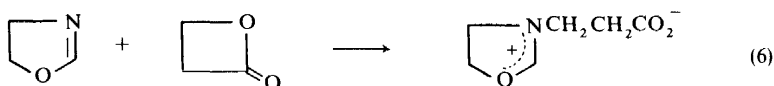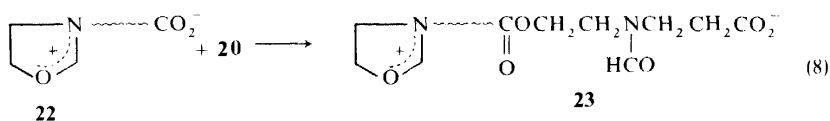*Figure 12a* shows the time–conversion and the time–molecular weight

Figure 12. OZO–BPL copolymerization. a: Copolymer yields versus time and molecular weight versus time, b: Number of copolymer molecule versus time.

curves. The monomer feed ratio was 1:1. From the amount and molecular weight of copolymer, the number of copolymer molecules was calculated; this is regarded as the number of active species. The curve in *Figure 12b* indicates the change of the number of propagating species with time, which increases rapidly in the early stages and then remains constant in the later stages of polymerization.

The OZO–BPL copolymerization is strongly characterized by the spontaneousness and the incorporation of two monomers in an alternate order. The following scheme of reactions is quite compatible with several experimental observations.

(6)

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$$20 \quad + \quad 20 \quad \longrightarrow \quad \underset{21}{\left[\overset{+}{\underset{O}{N}}\right]} \overset{\qquad}{\underset{\underset{HCO}{|}}{N}} CH_2CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_2\overset{\qquad}{\underset{HCO}{N}}CH_2CH_2CO_2 \qquad (7)$$

$$\underset{22}{\left[\overset{+}{\underset{O}{N}}\right]} \sim\sim\sim CO_2^- \quad + 20 \quad \longrightarrow \quad \underset{23}{\left[\overset{+}{\underset{O}{N}}\right]} \sim\sim\sim \overset{\overset{O}{\|}}{C}OCH_2CH_2\overset{\qquad}{\underset{HCO}{N}}CH_2CH_2CO_2^- \qquad (8)$$
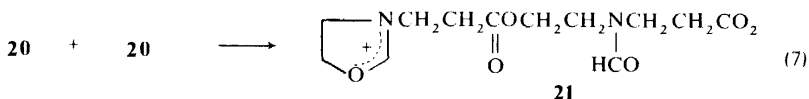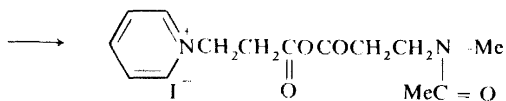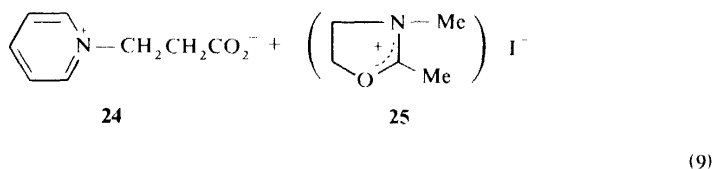
First, a betaine **20** is formed from OZO and BPL [equation (6)], and then, the reaction between two molecules of **20** produces a zwitterion **21**, in which the carboxylate group of one betaine makes a nucleophilic attack on to the 5-methylene group of oxazolinium ring of another betaine molecule. A dimetic zwitterion **21** is the smallest propagating species, whose carboxylate group is a stronger nucleophile than **20** because the carboxylate group in **21** is located far from the site of positive change. Successive addition of **20** to the carboxylate group of the growing species (**21** and **22**) constitutes the propagation step.

The formation of betaine is the rate-determining step. Betaine reacts with the carboxylate group of **22** as soon as it is formed. The change of the concentration of propagating species with the reaction time (*Figure 12b*) is well explained by the above scheme, i.e. equation (6) occurs mainly at an early stage of polymerization where the concentration of the propagating species carrying a stronger nucleophile of carboxylate is low. By equation (6), the concentration of propagating species (**21, 22**) is increased. As the concentration of propagating species is increased, the fraction of betaine consumption by its reaction with **22** [equation (8)] is continuously increased and the fraction of the reaction of equation (7) is decreased. At a latter stage of polymerization, betaine is consumed exclusively by its reaction with **22**, where the concentration of total propagating species remains unchanged.

The above scheme is supported by several experimental facts. First, aprotic polar solvent is favourable because it increases the rate of formation of betaine, an ionic species, from neutral molecules of the two monomers. Second, equations (7) and (8) are rationalized by the following model reaction (equation (9)).

$$\underset{24}{\left[\overset{+}{N}\right]}-CH_2CH_2CO_2^- \quad + \quad \left(\underset{25}{\left[\overset{+}{\underset{O}{N}}\overset{-Me}{\underset{Me}{}}\right]}\right) \quad I^-$$

$$(9)$$

$$\longrightarrow \quad \left[\overset{+}{N}\right]\overset{\qquad}{\underset{I^-}{N}}CH_2CH_2\overset{\overset{O}{\|}}{C}OCOCH_2CH_2\overset{\qquad}{\underset{MeC=O}{N}}-Me$$

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The isomerization ring-opening of 2,3-dimethyl-2-oxazolinium iodide **25** by the nucleophilic attack of carboxylate of the pyridine betaine of BPL **24** was established by n.m.r. spectroscopy.

According to the scheme, the oxazolinium and carboxylate ends of the propagating species may remain active even after all monomers have been consumed. This assumption has been rationalized by a two-stage polymerization scheme. At the first stage, an equimolar mixture of OZO and BPL was polymerized almost completely. Then, the second feed of an equimolar mixture was added to the system of the first polymerization mixture, and the second-stage polymerization was allowed to continue. *Figure 13* shows a linear
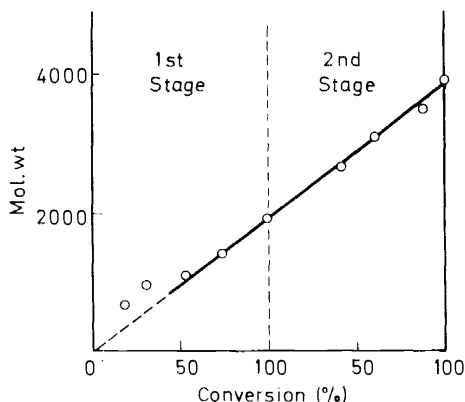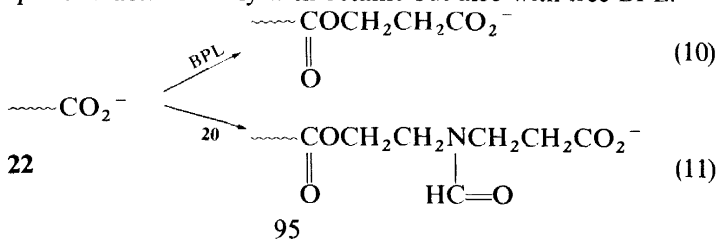

Figure 13. OZO–BPL copolymerization. Percent conversion versus molecular weight in the two stage polymerization.

relationship between the molecular weight and the percent conversion which holds throughout the course of the two-stage polymerization. This result means that the growing macrozwitterions present at the end of the first stage continue to grow throughout the second stage.

The intermolecular and intramolecular reactions between the oxazolinium ring and carboxylate group of the macrozwitterion take place slowly. After all monomer had been consumed, a slow increase of molecular weight of the copolymer was observed, which is understandable by assuming the intermolecular reaction of macrozwitterions.

At small feed ratios of OZO, the copolymer product was not the 1:1 alternating one but contains more than 50 per cent of BPL unit (*Figure 10*). This fact is also compatible with the above scheme. The carboxylate end of the growing species reacts not only with betaine but also with free BPL:

$$\sim\!\!\sim\!\!COCH_2CH_2CO_2^-$$
$$\overset{\|}{O} \qquad (10)$$

$$\sim\!\!\sim\!\!CO_2^-$$
$$\mathbf{22}$$

$$\sim\!\!\sim\!\!COCH_2CH_2NCH_2CH_2CO_2^-$$
$$\overset{\|}{O} \qquad \overset{|}{HC}\!\!=\!\!O \qquad (11)$$

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The reaction of **22** with BPL corresponds to the propagation step of the well-known anionic polymerization of BPL. Two propagation processes, (10) and (11), are in competition with each other. The relative rates of these two competing propagation steps are determined by the concentrations and reactivities of these two electrophiles. When the fraction of OZO in the monomer mixture is small, the propagation to BPL takes place to some extent.

A new concept of the OZO–BPL copolymerization suggests many other possible combinations of copolymerization of cyclic imino-ethers with various types of monomers. Comonomers which have been successfully copolymerized spontaneously with substituted and unsubstituted cyclic imino-ethers are substituted lactones, cyclic anhydrides of bis-carboxylic acids, sulpholactones (sultones), and acrylic and methacrylic acids[16, 25, 26]. Several combinations among these gave 1:1 alternating copolymers. The following are examples.

An equimolar mixture of OZO and succinic anhydride **26** in acetonitrile gave the 1:1 alternating copolymer **27**. A betaine of oxazolinium-carboxylate **28** may reasonably be considered as key intermediate[26].
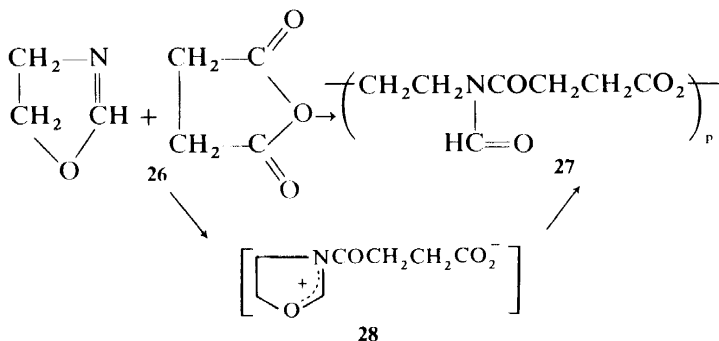
An equimolar mixture of OZO and acrylic acid in acetonitrile 50–60 °C gave a copolymer whose structure was the same as that of the 1:1 alternating copolymer of OZO and BPL[16]. This is an interesting example of copolymerization between cyclic and olefinic monomers. The first step will be the nucleophilic addition of OZO to an electron-poor double-bond of acrylic acid to form a zwitterion **29**, which in turn is converted into another betaine **30** by proton transfer. The betaine **30** is the same as that produced from OZO and BPL, which is a key intermediate for the 1:1 alternating copolymerization.

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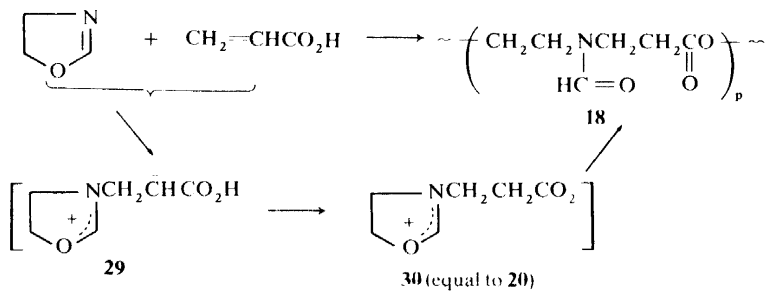
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