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### Polymerization of Salts of 2-Alkenyl-2-Oxazolines and Their Homologs

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## POLYMERIZATION OF SALTS OF 2-ALKENYL-2-OXAZOLINES AND THEIR HOMOLOGS

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### ABSTRACT

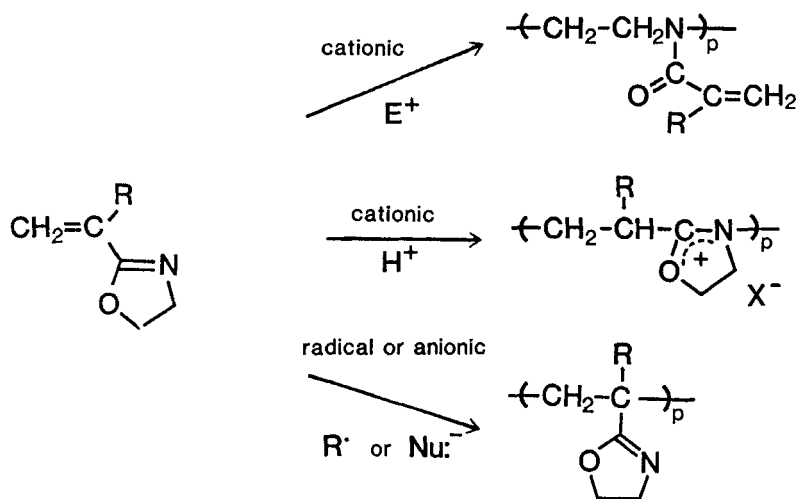
The present paper describes a new type of polymerization of 2-vinyl-2-oxazoline and 2-vinyl-5,6-dihydro-4*H*-1,3-oxazine and their salts. When these two imino ether monomers are allowed to react with Meerwein reagents or super acid esters, *N*-alkylation takes place first, followed by polymerization through the opening of vinyl groups to give poly[(2-oxazolinium-2-yl)ethylene] and poly[(5,6-dihydro-4*H*-1,3-oxazinium-2-yl)ethylene], respectively. With the corresponding 2-isopropenyl homologs, 2-isopropenyl-2-oxazoline and 2-isopropenyl-5,6-dihydro-4*H*-1,3-oxazine, stable *N*-alkylated salts are obtained, which were subjected to radical and base-catalyzed polymerizations. From the above results the reactivities of the salts are considered in terms of their ring size and the substituents on the olefinic functions.

### INTRODUCTION

Cyclic imino ether is one of the most interesting heterocyclic compounds that has been studied in the fields of both organic synthesis and polymerization chemistry. In the past decades the ring-opening polymerizations of these cyclic imino ethers have been studied extensively [1-3]. 2-Oxazoline (OZO) of a five-membered ring system and 5,6-dihydro-4*H*-1,3-oxazine (OZI) of a six-membered ring system are generally polymerized by cationic initiators,

producing poly[(*N*-acyl)iminoethylene] and poly[(*N*-acyl)iminotrimethylene], respectively. In these polymerizations the *N*-alkylated salts are known as the propagating species. As model compounds to simulate such active species, the *N*-alkylated salts were once prepared by the reactions of OZO and OZI with some specific protonating and alkylating agents.

Another active study of cyclic imino ether is the polymerization of 2-alkenyl derivatives of cyclic imino ethers. These monomers can be polymerized by various initiators to different types of polymers as shown below [4-7].



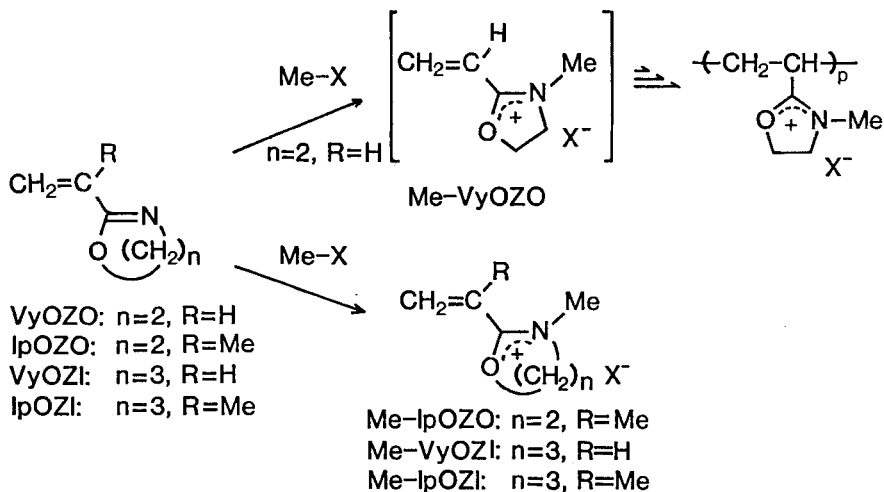
However, the corresponding salts have not yet been prepared for 2-alkenyl derivatives of cyclic imino ethers, probably due to their instability.

Based on this background, the preparation and polymerization of *N*-alkylated salts of 2-alkenyl derivatives of cyclic imino ethers are interesting subjects for study. Because of their salt structure, the electron-withdrawing and conjugative properties are thought to be intensified, and the olefinic reactivities should be greatly changed. In the present paper our recent investigations of the polymerization of the salts of these cyclic imino ethers are summarized.

### PREPARATION OF CYCLIC IMINO ETHER SALTS

*N*-Methylation of four monomers, i.e., 2-vinyl- (Me-VyOZO) and 2-isopropenyl-3-methyl-2-oxazolinium salts (Me-IpOZO) and 2-vinyl- (Me-VyOZI) and 2-isopropenyl-3-methyl-5,6-dihydro-4*H*-1,3-oxazinium salts (Me-IpOZI), was

attempted by the alkylation of these cyclic imino ethers with Meerwein reagents or super acid esters, and it was found that two different types of products were produced.



For 2-vinyl-2-oxazoline (VyOZO) with a vinyl functionality, the *N*-methylated salt was not isolated, but a white or a slightly yellow polymeric material was obtained almost quantitatively (*vide infra*) [8]. For 2-vinyl-5,6-dihydro-4*H*-1,3-oxazine (VyOZI) a similar "spontaneous" polymerization also proceeds at 0°C in Et<sub>2</sub>O, but the monomeric salt can be isolated when the reaction is carried out at -30°C [9]. (See Table 1.)

On the contrary, with the corresponding 2-isopropenyl derivatives, i.e., 2-isopropenyl-2-oxazoline (IpOZO) and 2-isopropenyl-5,6-dihydro-4*H*-1,3-oxazine (IpOZI), the stable salts were easily prepared in high yields by reaction with the alkylating agents at 0°C [10, 11].

These salts are soluble in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, DMF, and other aprotic polar solvents. Their structures were reasonably well established by both spectroscopic and elemental analyses.

### SPONTANEOUS POLYMERIZATION OF 2-VINYL CYCLIC IMINO ETHERS UPON ALKYLATION

When the alkylation of VyOZO with a strong alkylating agent was tried at 0°C in Et<sub>2</sub>O and in CH<sub>2</sub>Cl<sub>2</sub>, a white or a slightly yellow material precipitated. The product was obtained almost quantitatively and was found to

TABLE 1. Preparation of Cyclic Imino Ether Salts

Cyclic imino ether	Alkylating agent	Feed ratio <sup>a</sup>	Solvent	Temperature, °C	Product	
					Structure	Yield, % mp, b °C
IpOZO	FSO <sub>3</sub> Me	1.0	CH <sub>2</sub> Cl <sub>2</sub>	0	Me- <i>Ip</i> OZO	91 60-63
IpOZO	Me <sub>3</sub> OBF <sub>4</sub>	1.0	CH <sub>2</sub> Cl <sub>2</sub>	0	Me- <i>Ip</i> OZO	93 82
VyOZI	CF <sub>3</sub> SO <sub>3</sub> Me	0.53	Et <sub>2</sub> O	-30	Me- <i>Vy</i> OZI	94 55
IpOZI	CF <sub>3</sub> SO <sub>3</sub> Me	1.0	Et <sub>2</sub> O	0	Me- <i>Ip</i> OZI	89 Liquid

<sup>a</sup>Molar ratio of cyclic imino ether to alkylating agent.

<sup>b</sup>Determined by DSC endotherms under a nitrogen atmosphere.

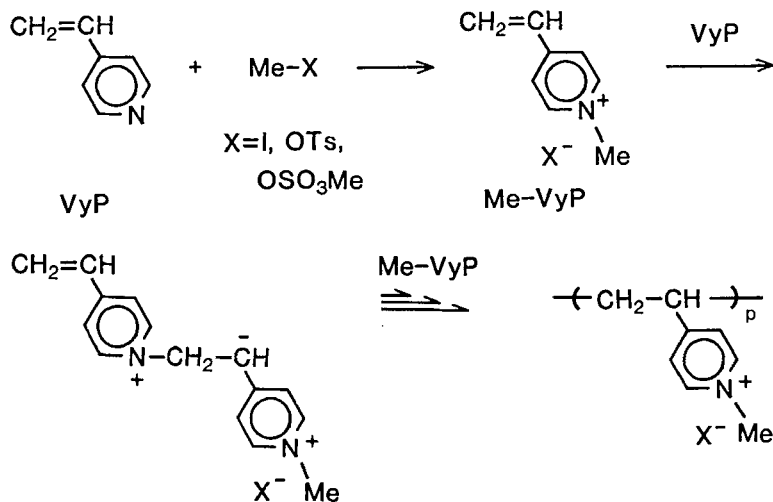
be a polymer of the structure of poly[1-(3-methyl-2-oxazolinium-2-yl)ethylene] [8]. The results are summarized in Table 2.

The properties of the products varied a little according to the gegenanion  $X^-$ . In general, the products are soluble in aprotic polar solvents such as  $\text{CH}_3\text{CN}$ , DMF, and DMSO. The molecular weight of the polymer was considered to be low, judging from the values of relative viscosity in DMF solution containing 2 wt%  $\text{NaBF}_4$ .

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR data are taken to indicate that the structure of the vinyl-polymerized chain has the 3-methyl-2-oxazolinium pendent group in every repeating unit.

An analogous polymerization also proceeded when the alkylation reaction of VyOZI was carried out in  $\text{CH}_2\text{Cl}_2$  or in  $\text{Et}_2\text{O}$  at  $0^\circ\text{C}$ .

The mechanism of the present polymerization should be considered in connection with the so-called "spontaneous" polymerization of vinylpyridines [12-17]. In the polymerization of 2- and 4-vinylpyridines, the *N*-alkylation of the monomer causes vinyl polymerization via an anionic mechanism. The free monomer remaining in the system functions as the initiator to add vinylpyridinium, producing an anionic propagating species.



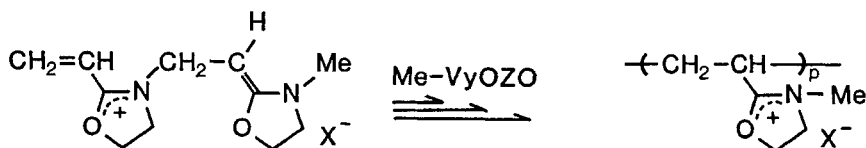
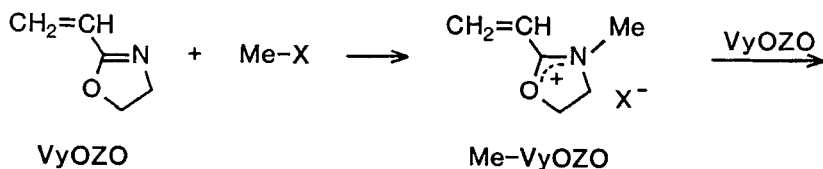
In order to clarify the reaction mechanism of the present "spontaneous" polymerization of VyOZO, the reaction was carried out in the presence of various additives [8]. Benzoquinone did not inhibit the polymerization. Styrene and methyl methacrylate were not incorporated in the polymer product. The addition of pyridine gave rise to the production of polymer

TABLE 2. Polymerization of 2-Vinyl Cyclic Imino Ethers on Alkylation

No.	Cyclic imino ether	Alkylating agent	Feed ratio <sup>a</sup>	Solvent	Temperature, °C	Yield, %	Product
							$\eta_{sp}/c$ , <sup>b</sup> dL/g
1	VyOZO	FSO <sub>3</sub> Me	0.84	CH <sub>2</sub> Cl <sub>2</sub>	0	83	0.044
2	VyOZO	FSO <sub>3</sub> Me	0.84	Et <sub>2</sub> O	0	88	0.043
3	VyOZO	CF <sub>3</sub> SO <sub>3</sub> Me	0.88	CH <sub>2</sub> Cl <sub>2</sub>	0	74	0.020
4	VyOZO	Me <sub>3</sub> BF <sub>4</sub>	0.84	CH <sub>2</sub> Cl <sub>2</sub>	0	100	0.038
5	VyOZO	Et <sub>3</sub> BF <sub>4</sub>	0.84	CH <sub>2</sub> Cl <sub>2</sub>	0	96	0.030
6	VyOZI	FSO <sub>3</sub> Me	0.53	CH <sub>2</sub> Cl <sub>2</sub>	-30	94	0.037 <sup>c</sup>
7	VyOZI	CF <sub>3</sub> SO <sub>3</sub> Me	0.53	CH <sub>2</sub> Cl <sub>2</sub>	0	94	0.043 <sup>c</sup>
8	VyOZI	CF <sub>3</sub> SO <sub>3</sub> Me	0.53	Et <sub>2</sub> O	0	92	0.062 <sup>c</sup>

<sup>a</sup>Molar ratio of cyclic imino ether to alkylating agent.<sup>b</sup>In 2% NaBF<sub>4</sub>-DMF solution at 30°C.<sup>c</sup>Intrinsic viscosity.

having a pyridinium end group. The effects of the above additives are taken to exclude the possibilities of radical and cationic mechanisms. In this polymerization, Me-VyOZO salt, which is produced by alkylation, is the key intermediate. It is reactive and rapidly enters into polymerization as soon as it is formed. The polymerization is initiated by a small amount of free monomer, which remains unreacted.



The intermediacy of *N*-methylated salt is supported by the results with Me-VyOZI. In the case of Me-VyOZI, the *N*-methyl salt was isolated, which polymerized during its recrystallization. In this case, too, a trace amount of contaminant free monomer may be responsible for the initiation [9].

### BASE-CATALYZED POLYMERIZATION OF *N*-METHYL SALTS

The reactivity of Me-VyOZI has been confirmed by the results of the polymerization of Me-VyOZI with several bases as initiator [9]. As shown in Table 3, pyridine, triethylamine, triphenylphosphine, and tetramethylammonium propionate were effective for the polymerization under mild conditions, while water did not initiate the polymerization even at 50°C.

Contrary to the vinyl-type salts, the polymerization reactivities of isopropenyl-type salts toward bases are quite low [10, 11]. Triethylamine is effective as an initiator for the polymerization of Me-IpOZO and Me-IpOZI. However, the polymerization required a higher temperature (room temperature or 80°C), and the yields of the product were not high. The structure of the polymer resulting from Me-IpOZO was determined as poly[1-(2-oxazolinium-2-yl)-1-methylethylene] from <sup>1</sup>H and <sup>13</sup>C NMR and IR data. The structure



TABLE 3. Base-Catalyzed Polymerization of Cyclic Imino Ether Salts

Run	Monomer	Initiator		Solvent	Temperature, °C	Time, h	Yield, %	[ $\eta$ ], <sup>a</sup> dL/g
		Type	mol%					
1	Me-VyOZI	Et <sub>3</sub> N	1.0	MeCN	RT	1	94	0.10
2	Me-VyOZI	Pyridine	1.0	MeCN	RT	1	67	0.12
3	Me-VyOZI	Ph <sub>3</sub> P	1.0	MeCN	RT	1	81	0.038
4	Me-VyOZI	EtCO <sub>2</sub> NMe <sub>4</sub>	1.0	MeCN	RT	1	92	0.063 <sup>b</sup>
5	Me-IpOZO	Et <sub>3</sub> N	5.0	DMF	80	20	10	0.033 <sup>b</sup>
6	Me-IpOZI	Et <sub>3</sub> N	10.0	DMF	80	100	28	— <sup>c</sup>

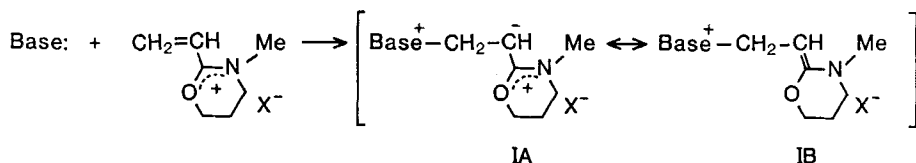
<sup>a</sup>In 2% NaBF<sub>4</sub>—DMF solution at 30°C.<sup>b</sup>Reduced viscosity at [C] = 0.12 g/dL in 2% NaI—CH<sub>3</sub>CN solution at 30°C.<sup>c</sup>Partially insoluble in DMF.

of the polymeric product from Me-IpOZI was complicated due to the concurrent ring-opening of the oxazinium ring.

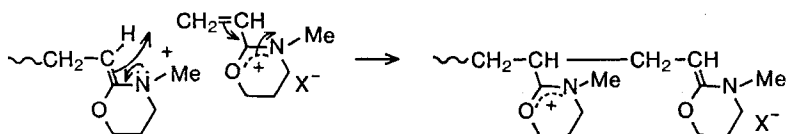
### MECHANISM OF THE BASE-CATALYZED POLYMERIZATION

The mechanism of the present base-catalyzed polymerization of Me-VyOZI and the polymerizations of VyOZO and VyOZI upon alkylation should be considered on a common basis since the latter is assumed to proceed after the formation of its *N*-methyl salt. The probable scheme is shown below. Initiation is the attack of a base on the vinyl group of the methylated salt. In the polymerization on alkylation, free monomer itself acts as a base initiator. Species I thus produced is stabilized by the resonance of two structures, i.e., the zwitterionic form IA and the ene form IB. If the propagation proceeds through the zwitterionic form, the general anionic chain polymerization would proceed by ordinary addition of the vinyl monomers to the anionic polymer end. In the present polymerization, however, such an anionic center is not improbable. Instead, the ene form is considered as the propagating species. It is a ketene *N,O*-acetal, a kind of enamine, which is generated by the so-called 1,4-type conjugative addition of the base to  $\text{CH}_2=\text{CH}-\text{C}=\text{N}^+$  of the methylated salt. During propagation, a similar 1,4-addition is repeated successively between the propagating terminal ketene *N,O*-acetal and the salt of the monomer.

Initiation:

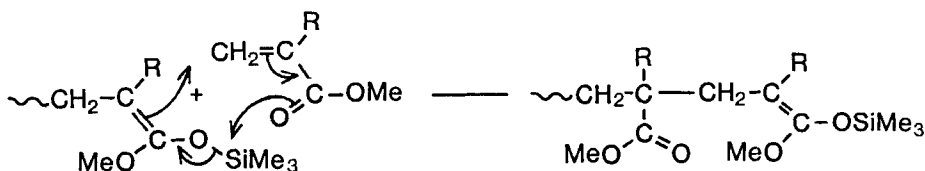


Propagation:



It is of interest to note the similarity of the reaction form between the above propagation and that of group-transfer polymerization [18, 19]. In group-transfer polymerization the structure of the active growing species is that of a

trimethylsilyl-substituted ketene acetal, which is quite similar to the ketene *N,O*-acetal in our new polymerization.



In ordinary anionic polymerization, propagation proceeds via the nucleophilic attack of a carbanionic chain end on an olefin bond of a neutral monomer. By contrast, the propagation in the present "base-catalyzed" polymerization proceeds via a conjugative attack of neutral (covalent), but nucleophilic, ketene *N,O*-acetal at the propagating end on a monomer having a positive charge.

Generally, vinyl polymerizations are classified into three groups, i.e., radical, anionic, and cationic, based on the type of their growing species, although one cannot classify the present and the group-transfer polymerizations as anionic polymerizations because they proceed by covalent nucleophilic propagation ends instead of an anionic propagating species.

It is therefore proposed that the additional polymerizations are to be classified into three new groups on the basis of the nature of the propagating species, i.e., polymerizations via radical, electrophilic, and nucleophilic propagating species. Concerning nucleophilic polymerization via nucleophilic propagating species, three types are possible according to the nature of the reaction. The first is the propagation between an anionic propagating end and a neutral monomer (ion-dipole reaction). The usual anionic polymerizations belong to this type. The second one is the reaction of a neutral, but nucleophilic, propagating species with a neutral monomer (dipole-dipole reaction). Group-transfer polymerization and the so-called coordinating polymerizations of olefins and epoxides are in this category. The last one is the reaction of a neutral (covalent) propagating species with a positively charged monomer (dipole-ion reaction). The present base-catalyzed polymerization is the first example of the third type of polymerization.

When the five-membered monomer *VyOZO* was reacted with an alkylating agent at 0°C in Et<sub>2</sub>O, spontaneous polymerization occurred, but no reaction took place at temperatures below -20°C. Therefore, the corresponding monomeric salts Me-*VyOZO* could not be isolated. In the case of *VyOZI*, spontaneous polymerization also occurred at 0°C in Et<sub>2</sub>O, but the salt Me-*VyOZI* was the sole product at -30°C. Thus, the oxazine group is assumed to be more reactive to the alkylating agent.

TABLE 4. Basicity and Nucleophilicity of Cyclic Imino Ethers

Cyclic imino ether		$pK_a^a$	Rate constant of the Menshutkin reactions with MeOTs, <sup>b</sup> $\times 10^4$
2-Substituent	Ring size		
H	5	5.58	0.98
CH <sub>2</sub> =CH	5	5.00	—
H	6	7.20	11.8
CH <sub>2</sub> =CH	6	7.43	—

<sup>a</sup>At 25°C.

<sup>b</sup>In acetonitrile at 40°C, data from Ref. 20.

Judging from the  $pK_a$  values of both monomers (Table 4) and the kinetic results of the cationic ring-opening polymerization of cyclic imino ethers [20], 5,6-dihydro-4*H*-1,3-oxazine appears to have the higher nucleophilicity toward the alkylating agents, i.e., ~10-fold that of 2-oxazoline.

Thus the alkylation of VyOZI can proceed even at a lower temperature. In addition, it is also assumed that the 1,3-oxazinium ion is much stabler than the oxazolinium ion if they contain the same substituent groups. It is therefore assumed that the stability of Me-VyOZI is higher than that of Me-VyOZO. On the basis of these facts, the success in isolating Me-VyOZI, the base-catalyzed polymerizability, and the reactivity in "spontaneous" polymerization are well understood.

In the cases of IpOZO and IpOZI, the corresponding salts, Me-IpOZO and Me-IpOZI, were readily isolated by similar alkylation at 0°C. They are stable at room temperature. Thus, the isopropenyl group is assumed to be less reactive toward polymerization due to its steric hindrance (*vide infra*).

### RADICAL POLYMERIZABILITY OF METHYLATED SALTS

To clarify the vinyl polymerizability of these *N*-methylated salts, the radical polymerization of the salts was further investigated [9, 20]. As shown in Table 5, Me-VyOZI is smoothly polymerized by using azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) as the initiator. The resulting polymer is a white solid which was identified as poly[1-(3-methyl-5,6-dihydro-4*H*-1,3-oxazin-2-yl)ethylene], the polymer structure being the same as that of the

TABLE 5. Radical Polymerization of Cyclic Imino Ether Salts

Run	Monomer	Initiator		Solvent	Temperature, °C	Time, h	Yield, %	$[\eta]$ , <sup>a</sup> dL/g
		Type	mol%					
1	Me-VyOZI	AIBN	1	MeCN	60	5	63	0.18
2	Me-VyOZI	BPO	1	MeCN	60	6	77	0.15
3	Me- <i>Ip</i> OZO	AIBN	3	DMF	60	50	11	0.043 <sup>b</sup>
4	Me- <i>Ip</i> OZO	AIBN	2	Bulk	70	10	0	—
5	Me- <i>Ip</i> OZO	<sup>c</sup>		Bulk	RT	24	7	—

<sup>a</sup>In 2% NaBF<sub>4</sub>-DMF solution at 30°C.

<sup>b</sup>Reduced viscosity at  $[C] = 0.12$  g/dL in 2% NaI-CH<sub>3</sub>CN solution at 30°C.

<sup>c</sup><sup>60</sup>Co radiation;  $5 \times 10^5$  rd/h.

product of the base-catalyzed polymerization of Me-VyOZI. In every run of Table 5 the yield of the polymer was rather high and its viscosity of DMF containing NaBF<sub>4</sub> was 0.15-0.20. The latter value seems to be a little higher than that of the product of both base-catalyzed (below 0.12) and "spontaneous" polymerizations (below 0.06).

The radical polymerization of Me-IpOZO gave polymer with a low solution viscosity in poor yield under the usual radical polymerization conditions with AIBN as initiator. A considerable amount of monomer was left unreacted.

The bulk polymerization of Me-IpOZO in the melt (Run 4) produced no polymeric material. In the experiment of irradiation polymerization (Run 5), the crystalline salt of Me-IpOZO was exposed to <sup>60</sup>Co at  $5 \times 10^5$  rd/h. The color of the salt changed from white to brown after 1 d of irradiation, resulting in only a small amount of polymeric product.

A trial of the radical polymerization of Me-IpOZI was a failure. The reactions were carried out at temperatures as high as 100°C by changing the molar ratio of the initiators (AIBN or BPO) from 0.5 to 5.5%. However, no polymerization took place, and the monomer Me-IpOZI was recovered quantitatively in all cases.

As described above, Me-IpOZO shows poor vinyl polymerizability in both radical and base-catalyzed polymerizations, and Me-IpOZI shows no vinyl polymerizability. These results were interesting when compared with those obtained with the parent monomers of IpOZO and IpOZI. For example, the radical polymerization of IpOZO with AIBN as initiator (0.5 mol%) in DMF affords poly[1-(2-oxazolin-2-yl)-1-methylethylene] with high molecular weight in 72% yield under relatively mild conditions, 60°C for 50 h.

Reasons for the poor polymerizability of Me-IpOZO might be the electrostatic repulsion between oxazolinium cations and the steric hindrance of the isopropenyl group. Concerning the steric hindrance, it is to be relevantly noted that *N,N*-disubstituted methacrylamide (corresponding to Me-IpOZO and Me-IpOZI) is not polymerizable, whereas *N*-monosubstituted methacrylamide (corresponding to IpOZO and IpOZI) and *N,N*-disubstituted acrylamide (corresponding to Me-VyOZO and Me-VyOZI) can be polymerized. The chain propagation of the disubstituted methacrylamide was found to be sterically hindered [21-23].

The difference in polymerizability between Me-IpOZO and Me-IpOZI could also be attributed to steric crowdedness around the olefinic groups. The steric hindrance in Me-IpOZO is partially reduced because the strained 5-membered oxazolinium ring forces the *N*-methyl group to keep away from the isopropenyl substituent.

As in the case of VyP, these 2-alkenyl derivatives of cyclic imino ethers are

polymerized by super acids such as fluorosulfonic and trifluoromethanesulfonic acids. However, the polymerization is not clean due to proton transfer from the ammonium nitrogen to the nucleophilic (basic) site of the propagating species [11].

In summary, the order of reactivity of *N*-methyl salts is considered to be Me-VyOZO > Me-VyOZI >> Me-IpOZO > Me-IpOZI. These reactivity difference can be interpreted consistently by their steric factors and the nucleophilicities of the parent cyclic imino ethers.

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