

# SALT EFFECTS ON VINYL POLYMERIZATION—A BOUNDARY STUDY OF ORGANIC AND INORGANIC CHEMISTRY

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## ABSTRACT

Vinyl polymerization is often affected by the addition of metal salts. A common example of metal salt effects is already seen in redox initiation systems. In this paper the salt effects on the propagation process of vinylpyridine and *N*-vinylimidazole, and the direct redox initiation of vinylpyridine, *N*-vinylimidazole and *N*-vinylcarbazole are discussed.

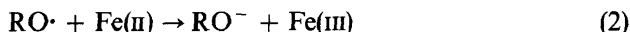
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## INTRODUCTION

INTERMEDIATE fields of chemistry which are not included in the traditional territory of both organic and inorganic chemistry are rapidly coming to the fore. When one deals with organic reactions, it is immediately realized that numerous reactions are influenced by the presence of metal salts. The specific catalytic effects of metal salts should be attributed to interactions between organic compounds and metal salts. What kind of electronic as well as steric effects are brought about on the ligand when organic molecules are coordinated? The answer to this question is essential for an understanding of the catalytic action of metal salts in organic reactions. The present trend of coordination chemistry is mostly directed to understanding the reactivity of the central metal ion, stereochemistry, nature of coordination bond and so on. In general, no emphasis is placed on the reactivity of coordinated organic ligands.

As a branch of organic reactions, vinyl polymerization is often affected by the addition of metal salts. For example, redox inert metal salts such as those of zinc<sup>1</sup> and lithium<sup>2</sup> are known to affect the rate of radical propagation in certain cases. Complex formation of metal salts with monomer and/or growing radical would be the cause of the effects due to salts. Further insight into the salt effect as to why complex formation is so influential remains unexplained. The problem should be dealt with from the viewpoint of reactivities of coordinated organic ligands. A more common example of metal salt effects is seen in redox initiated systems. The redox properties of transition metal salts are favourably utilized as promoters of redox initiator systems. The simplest redox pair of the peroxide-ferrous ion system is

expressed as follows :



This simple reaction scheme involves many useful suggestions. First, reaction 1 seems to be primarily an electron transfer process. The counterpart of the metal salt is not necessarily the peroxide or so-called initiator since removal or donation of an electron would produce a cation radical or an anion radical on an organic molecule, respectively, and such ion radicals could induce polymerization either by radical or ionic processes. Secondly, the movement of electrons should have a close connection with photochemistry. In particular, irradiation at the charge transfer band brings about electronic transmission corresponding to electron transfer between metal ion and ligand. Many redox processes both in organic and inorganic reactions are known to be induced under photoirradiation. Thirdly, redox reaction between radical and metal ion (reaction 2) is responsible for the retarding effects of metal salts in radical polymerization. Kinetic mechanistic studies of reactions between growing polymer radical and metal salt have been made. Both electron transfer<sup>3</sup> and ligand transfer<sup>4</sup> mechanisms were suggested depending upon the nature of the growing polymer radical and the metal complex.

In this report, the salt effects on the propagation process of vinylpyridine and vinylimidazole, and the direct redox initiation of vinylpyridine, *N*-vinylimidazole and *N*-vinylcarbazole are discussed.

## PROPAGATION

### Effects of zinc salts on homopolymerization of vinylpyridine

The basic nitrogen in vinylpyridine has strong coordinating properties towards various metal salts. For example, complexes of 4-vinylpyridine(4-VP), 2-vinylpyridine(2-VP) and 2-methyl-5-vinylpyridine(MVP) with Zn(II), Cd(II) and Hg(II) are separated as crystals and the mole ratios of amines to metal salts<sup>5</sup> are always 2:1. In solution, however, the monomer complexes will exist as mixtures of 1:1 and 2:1 complexes depending upon the stepwise stability constants and the concentrations of amine and metal salt. The complexed vinyl compounds naturally have different reactivities and the rates of polymerization ( $R_p$ ) of 4-VP, 2-VP and MVP are greatly affected by the presence of zinc acetate<sup>6</sup> as depicted in *Figure 1*. The trend of the salt effect on  $R_p$  differs strikingly for 4-VP, 2-VP and MVP. With 4-VP, the value of  $R_p$  levels off when the concentration of Zn(II) is well over that of 4-VP, indicating the completion of complex formation.

The approximately linear correlation between  $R_p$  and degree of polymerization as measured at different zinc acetate concentrations implies that the main effect of complex formation is to enhance the rate of propagation. The determination of absolute rate constants in somewhat different polymerization systems indicates that  $k_p$  is increased exclusively by the

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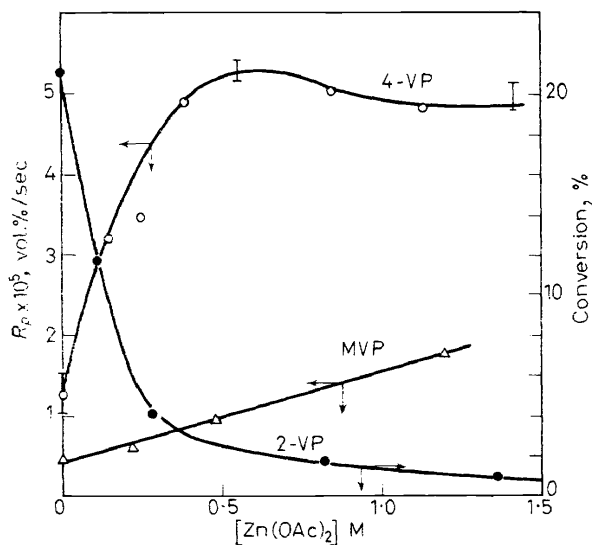


Figure 1. Polymerization of vinylpyridine in the presence of zinc acetate in DMF at 50°C. ○: [4-VP] = 0.43M, [AIBN] =  $1.22 \times 10^{-2}$ M, Δ: [MVP] = 0.43M, [AIBN] =  $1.22 \times 10^{-2}$ M, ▲: [2-VP] = 0.85M, [AIBN] =  $2.44 \times 10^{-2}$ M, polymerization for 8 h.

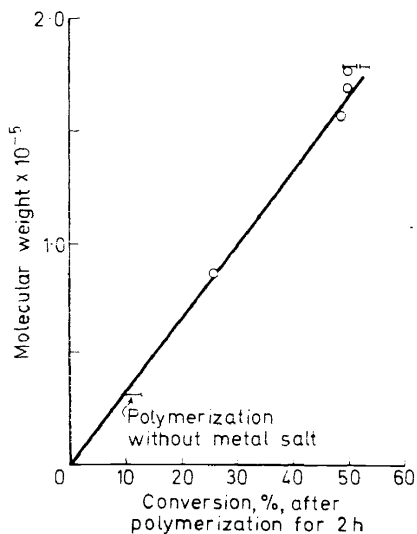


Figure 2. Plots of polymer yield versus molecular weight of poly 4-VP. [4-VP] and [AIBN]: constant;  $[\text{Zn}(\text{CH}_3\text{COO})_2]$ : variable.

addition of lithium chloride to acrylonitrile<sup>2</sup> or zinc chloride to methyl methacrylate<sup>1</sup>.

### Effects of zinc acetate on copolymerization of vinylpyridine and *N*-vinylimidazole with styrene

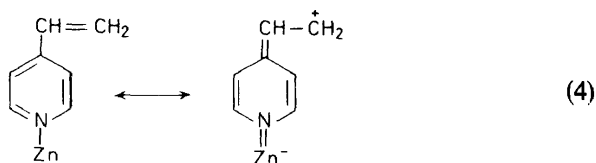
The changes in reactivity of active species and monomer can be conveniently examined by copolymerization. The results of copolymerization of vinylpyridine with styrene in the presence of a large excess of zinc acetate are set out in *Table 1*. A marked increase in monomer reactivity was observed for

*Table 1.* Copolymerization of VP with styrene in the concentrated solution of zinc acetate at 50°C. ( $M_1 = \text{VP}$ ,  $M_2 = \text{Styrene}$ )

$M_1$	$r_1$	$r_2$	$Q_1$	$e_1$
4-VP <sup>a</sup>	0.52 – 0.7	0.54 – 0.62	0.82	– 0.20
4-VP-Zn(II)	2.7 ± 0.5	0.08 ± 0.03	4.7	+ 0.44
2-VP <sup>a</sup>	0.9 – 1.81	0.55	1.30	– 0.50
2-VP-Zn(II)	3.35 ± 0.3	0.55 ± 0.15		$r_1 r_2 = 1.84$
MVP <sup>a</sup>	0.68 – 1.19	0.6 – 0.88	0.99	– 0.58
MVP-Zn(II)	2.0 ± 0.2	0.35 ± 0.05	1.75	– 0.26

<sup>a</sup> Data of copolymerization were taken from Ham.

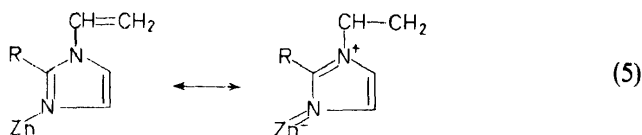
4-VP in the presence of zinc acetate while the monomer reactivity of MVP was not greatly changed. The enhanced  $Q$  value and the positive shift of the  $e$  value are indications that the electrons are in part donated from the monomer to the zinc salt and that the conjugation of monomer is enhanced as a result of the  $\pi$ -type interactions between monomer and zinc salt, although the interaction between pyridine-ring nitrogen and metal salt is essentially  $\sigma$ -type. A question arises as to whether Zn(II) having the  $3d^{10}$  ground state could effectively induce the  $d\pi-p\pi$  or  $p\pi-p\pi$  overlaps. So far as the  $3d^{10}$  state is concerned, the double bond nature of the coordination bond is difficult to accept. However, if the  $p$ -orbitals of zinc can be utilized, the  $p\pi-p\pi$  interaction seems to be energetically possible<sup>7</sup>. As will be described below, the  $\pi$ -type interactions are important even for zinc complexes. The different salt effects on 4-VP and MVP would then be attributed to the possibility of conjugation between zinc and the vinyl group. For MVP, the



contribution of resonance 4 is unlikely and consequently, the changes in  $Q$  and  $e$  values are smaller than those for 4-VP when the zinc salt is added to the polymerization system. The results of polymerization of 2-VP seem to be complicated by steric effects. The block nature of the copolymer ( $r_1 r_2 = 1.84$ ) may be interpreted if one assumes that two molecules of 2-VP are linked by the zinc salt and act as a bifunctional monomer to yield cyclic polymeriza-

tion. Assuming  $(2\text{-VP})_2\text{-Zn}$  to be a bifunctional monomer, the monomer reactivity ratios were calculated as  $r_1 = 1.1 \times 0.15$  and  $r_2 = 0.6 \times 0.15$ .

Copolymerization of 2-methyl-1-vinylimidazole(MVI) is also influenced by zinc acetate<sup>8</sup>. The complex-forming ability of the imidazole group is much stronger than that of the pyridine group. The stability data of the zinc complex of imidazole indicate that  $\text{ZnL}_2$  is the predominant species even when  $[\text{Zn}] \gg [\text{L}]$ , where L is imidazole ( $\log K_1 = 3.15$ ,  $\log K_2 = 2.95$  in  $0.058 \text{ N KCl}$  at  $25^\circ\text{C}$  where  $K_1$  and  $K_2$  are the first and the second stability constants of the imidazole-Zn(II) complexes, respectively<sup>9</sup>). The higher stability of the 2:1 complex of imidazole contrasts with the pyridine-zinc complex ( $\log K_1 = 1.41$ ,  $\log K_2 = -0.30$  in  $0.1 \text{ N KCl}$  at  $25^\circ\text{C}$ <sup>9</sup>). Consequently, the polymerization system of *N*-vinylimidazole in the presence of zinc acetate becomes heterogeneous due to crosslinking of polymer by the 2:1 complex formation. From copolymerization of MVI( $M_1$ ) with styrene( $M_2$ ),  $r_2$  is calculated to be  $20 \pm 4$  in the presence of zinc acetate in DMSO. Comparison of this reactivity ratio with the literature values<sup>10</sup> ( $r_1 = 0.069$ ,  $r_2 = 8.97$  where  $M_1$  is MVI) suggests a decrease in reactivity of MVI when the monomer is complexed. The change of monomer reactivity can be interpreted as a result of reduced conjugation brought about by complex formation.



### Spontaneous thermal polymerization of vinylpyridine<sup>11</sup>

Highly conjugated vinyl compounds such as styrene are known to polymerize thermally without an initiator. Complex formation brings about an enhanced conjugation of 4-VP and consequently the spontaneous thermal initiation is faster for the complexed 4-VP than for the free monomer. As shown in *Figure 3*, the ratio of  $R_p$  in the presence of zinc salt to that in the absence of zinc salt is 16 for the polymerization initiated by azobisisobutyronitrile (AIBN) in THF whereas this ratio is 47 for thermal polymerization. Since the participation of zinc salt in the decomposition of AIBN and the termination reaction is unlikely, the stronger salt effect in thermal polymerization would suggest the contribution of zinc salt to the initiation step. As expected from the lesser enhancement of conjugation for the MVP complex and the steric hindrance for the 2-VP complex, thermal initiation of these two monomers is scarcely affected in the presence of zinc salt.

Support for the radical nature of polymerization is obtained from the retardation of the initial rate of polymerization in the presence of air, the small effect of water and the inhibitory effect of DPPH.

### Infra-red spectroscopy of metal complexed vinyl compounds

Electronic effects caused by complex formation should reflect on the strength of chemical bonds in ligands. A comparison of the infra-red spectra of free and complexed vinylpyridine is given in *Table 2*<sup>6</sup>.

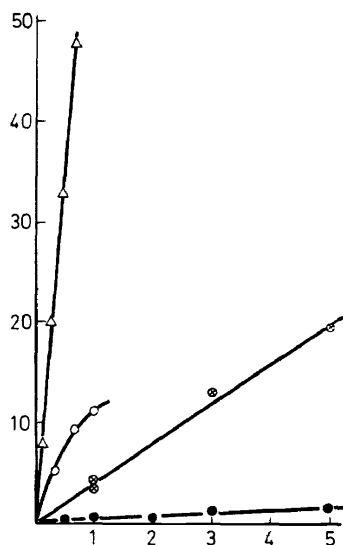


Figure 3. Effect of zinc acetate on thermal and AIBN-initiated polymerization of 4-VP in THF at 70°C. [4-VP] = 0.583M.  $\Delta$ : [AIBN] =  $10^{-3}$ M.; [Zn<sup>II</sup>] = 0.285M,  $\circ$ : [Zn<sup>II</sup>] = 0.285M,  $\otimes$ : [AIBN] =  $10^{-3}$ M.,  $\bullet$ : thermal polymerization.

Since infra-red spectra are influenced by the change of physical state, the comparison of liquid pyridine base with solid complexes is not always informative. However, the skeletal and stretching vibrations are mostly insensitive to environmental change and are chosen for comparison. The magnitude of the positive shifts of C=C and C=N skeletal vibrations of the pyridine ring are in the order, 4-VP  $\gtrsim$  2-VP > MVP. This order indicates

Table 2. Changes in infra-red spectra of vinylpyridines by complex formation

Sample	Skeletal vibration of pyridine ring, $\text{cm}^{-1}$			$\Delta \nu_{\text{total}}^a$ , $\text{cm}^{-1a}$	C=C stretching vibration, $\text{cm}^{-1a}$	$\Delta \nu$ , $\text{cm}^{-1}$
4-VP	1498,	1546,	1594		1632	
(4-VP) <sub>2</sub> -ZnCl <sub>2</sub>	1505,	1546,	1617	+ 30	1630	- 2
(4-VP) <sub>2</sub> -ZnBr <sub>2</sub>	1506,	1546,	1617	+ 31	1630	- 2
(4-VP) <sub>2</sub> -ZnI <sub>2</sub>	1506,	1545,	1616	+ 28	1632	0
2-VP	1472,	1561,	1587		1628	
(2-VP) <sub>2</sub> -ZnCl <sub>2</sub>	1484,	1561,	1606	+ 31	1634	+ 6
(2-VP) <sub>2</sub> -ZnBr <sub>2</sub>	1483,	1560,	1606	+ 29	1631	+ 3
(2-VP) <sub>2</sub> -ZnI <sub>2</sub>	1484,	1560,	1605	+ 29	1629	+ 1
MVP	1493,	1554,	1598		1632	
(MVP) <sub>2</sub> -ZnCl <sub>2</sub>	1501,	1564,	1601	+ 21	1632	0
(MVP) <sub>2</sub> -ZnBr <sub>2</sub>	1502,	1565,	1604	+ 26	1632	0
(MVP) <sub>2</sub> -ZnI <sub>2</sub>	1499,	1565,	1605	+ 24	1632	0

<sup>a</sup> Sum of shift for corresponding absorptions.

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that the shifts might be related to the mesomeric effect of the coordinated metal ion. The contribution of resonance structure shown by reaction 4 would increase the bond order of the C=C and C=N bonds and would then bring about blue shifts of these absorptions. This interpretation implies that the complex formation should affect the infra-red absorption of the C=C stretching vibration of the vinyl group as well. Although the shifts are small, the tendency to red shift is observed for the stretching vibration of the vinyl group of 4-VP complexes. The position of the corresponding absorption for the MVP complexes is the same as for free MVP as expected from the absence of a mesomeric effect. The 2-VP complexes show a blue shift of the stretching vibration. This is probably due to the steric interaction of the metal salt with the vinyl group, which more or less isolates the vinyl group from the pyridine ring.

In contrast to vinylpyridine, *N*-vinylimidazole loses conjugation between the vinyl group and imidazole group as shown by reaction 5. This resonance will hinder the conjugation represented by reaction 6 and the C=C stretching vibration of the isolated vinyl group appears in a higher wavelength region.



The magnitude of the blue shift is roughly proportional to the electronegativity of the central metal ion as shown in Table 3<sup>8</sup>.

Table 3. Shift of the stretching vibration of the vinyl group by complex formation

Sample	$\nu_{-\text{CH}=\text{CH}_2}$ , cm <sup>-1</sup>	$\Delta\nu$ , cm <sup>-1a</sup>	Electronic structure	Electro-negativity
EVI	1642			
EVI-HCl	1652	+ 10	1s <sup>0</sup>	2.1
(EVI) <sub>2</sub> ZnCl <sub>2</sub>	1650	+ 8	3d <sup>10</sup>	1.66
(EVI) <sub>2</sub> CoCl <sub>2</sub>	1649	+ 7	3d <sup>7</sup>	1.70
(EVI) <sub>2</sub> HgCl <sub>2</sub>	1647	+ 5	5d <sup>10</sup>	1.44
(EVI) <sub>2</sub> AgNO <sub>3</sub>	1645	+ 3	4d <sup>10</sup>	1.42

<sup>a</sup>  $\Delta\nu = (\nu) \text{ complex} - (\nu) \text{ free}$ .

### The $\pi$ - $\pi^*$ transition spectra of metal complexed vinyl compounds<sup>12</sup>

The electronic state of a vinyl compound is most directly observed by electronic spectroscopy. When a vinyl compound enhances conjugation by complex formation, the energy gap between the lowest vacant and highest occupied orbitals becomes smaller and the  $\pi$ - $\pi^*$  transition band shifts towards low energy regions. The results shown in Figure 4 agree very well with the expectation envisaged from the results of polymerization and infra-red spectroscopy. The large red shift of absorption of 4-VP as a result of complex formation confirms the contribution of resonance structures, reaction 4. The amounts of red shift of absorption for MVP and for the sterically hindered 2-VP are all quite small. The spectral change of MVI is also clear.

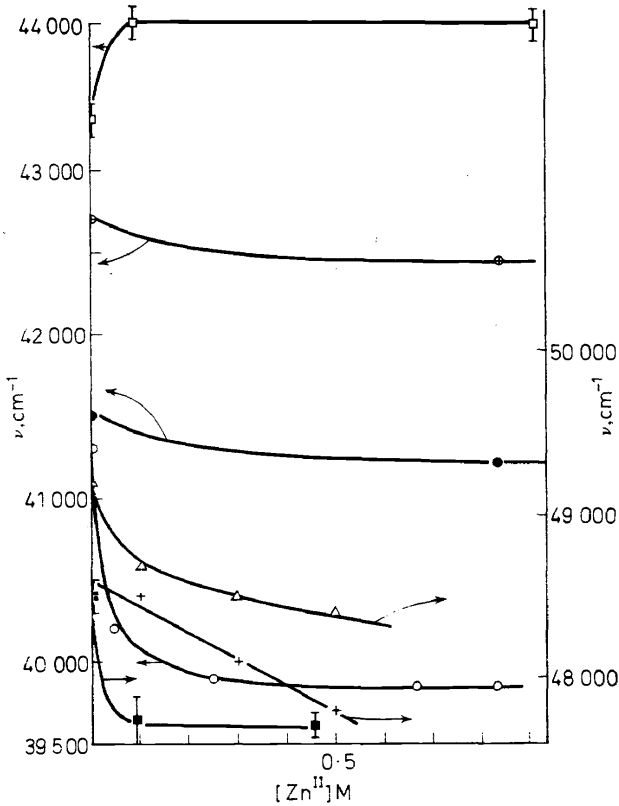


Figure 4. Effect of zinc salts on the  $\pi-\pi^*$  transition band of vinyl compounds. Solvent: methanol,  $[\text{vinyl compound}] = 10^{-4}$  to  $10^{-5}\text{M}$ .  $\text{Zn}(\text{OAc})_2$  added: 4-VP(○), MVP(●), 2-VP(⊕).  $\text{ZnCl}_2$  added: AN(△), MMA(×), MVI(□), MI(■).

The lower  $\pi-\pi^*$  transition energy of MVI than that of 2-methylimidazole is definitely attributed to the conjugation between the vinyl group and the imidazole ring. The conjugation of the imidazole ring itself is enhanced by complex formation as indicated by a red shift of the  $\pi-\pi^*$  transition band whereas the contribution of the vinyl group to the conjugation is reduced when the monomer is complexed. Consequently, the difference of the  $\pi-\pi^*$  transition energy between 2-methylimidazole(MI) and MVI tends to become smaller by addition of the zinc salt.

The spectroscopic investigation of methyl methacrylate (MMA) and acrylonitrile(AN) provides evidence to the postulate proposed by Imoto and Otsu<sup>13</sup> that these monomers are activated by complex formation.

The general theory of radical polymerization that the reactivity of monomers increases with the extent of conjugation seems to be valid for these metal complexed monomers. Correlation of the  $\pi-\pi^*$  transition energy and the

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Table 4. Changes in the  $\pi-\pi^*$  transition energy and reactivity of vinyl compounds due to complex formation with zinc salt

Monomer (M <sub>1</sub> )	complex	$Q_1^{\text{complex}}$	$(1/r_2)^{\text{complex}}$	Thermal polymerizability <sup>d</sup>
	$\nu_{\pi \rightarrow \pi^*}$ free - $\nu_{\pi \rightarrow \pi^*}$ cm <sup>-1</sup>			
4-VP	- 1450	5.7 <sup>a</sup>	6.8 ~ 7.8 <sup>a</sup>	Fast
MVP	- 300	1.8 <sup>a</sup>	1.7 ~ 2.5 <sup>a</sup>	Slow
2-VP	- 250	—	~ 1 <sup>a</sup>	None
MVI	+ 600	—	~ 0.41 <sup>a</sup>	None
AN	< - 800	—	—	Slow <sup>b</sup>
MMA	< - 700	3.8 ~ 9.0	3 ~ 12 <sup>c</sup>	None <sup>b</sup>

<sup>a</sup> M<sub>2</sub> is styrene.

<sup>b</sup> data by Imoto *et al.*

<sup>c</sup> M<sub>2</sub> is vinylidene chloride, data by Imoto *et al.*

<sup>d</sup> 4-VP, MVP, 2-VP and MVI: zinc acetate complex, AN and MMA: zinc chloride complex.

reactivities of vinyl compounds is summarized in Table 4. As another approach to the reactivities of metal complexed vinyl compounds, Hückel molecular orbital calculation can be applied assuming  $\pi$ -type interaction between vinyl compounds and metal salt. The calculated reactivities are in reasonable agreement with the observed reactivities<sup>7</sup>.

### INITIATION

#### Polymerization of vinylpyridine initiated by cupric acetate<sup>14</sup>

In the preceding section, partial charge transfer from vinylpyridine to zinc salt was discussed in various aspects. When a redox capable metal salt is coordinated to vinylpyridine, an electron would indeed be transferred from the ligand to the metal salt. This occurs in the cupric acetate initiated polymerization of 4-VP. Although the polymerization proceeds via a radical

Table 5. Solution polymerization of 4-VP initiated by cupric acetate monohydrate at 50°C.<sup>a</sup>

Solvent	$R_p \times 10^6$ , mole/l.-sec	Dielectric constant of solvent at 25°C
Bulk polymerization	3.29	12
Pyridine	0.715	12.3
Acetone	15.9	20.7
Methanol	15.5	32.6
Ethanol	2.76	24.3
n-Butanol	0.503	17.1
Dimethylformamide	1.06	
Benzene	0.0	2.3
Ethylene chloride	~ 0	10.4

<sup>a</sup> [Cu<sup>II</sup>] =  $1.0 \times 10^{-2}$  mole/l.; 4-VP/solvent = 1/1 by volume.

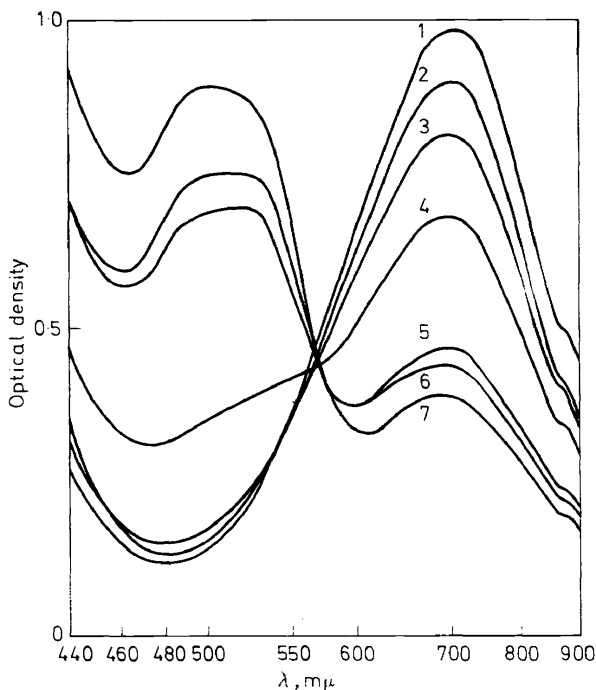


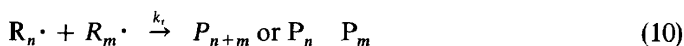
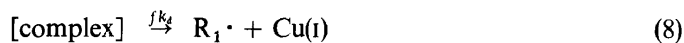
Figure 5. Visible absorption spectra of 2-vinylpyridine-methanol-cupric acetate system: (1) before reaction; (2) after reaction *in vacuo* at 50°C for 160 min; (3) after reaction *in vacuo* at 55°C for 160 min; (4) after reaction *in vacuo* at 65°C for 160 min; (5) after reaction *in vacuo* at 80°C for 93 min; (6) after reaction *in vacuo* at 70°C for 160 min; (7) after reaction *in vacuo* at 80°C for 160 min. 2-VP/methanol = 1/1 by volume;  $[Cu^{II}] = 1.0 \times 10^{-2}$  mole/l.

intermediate the rate of polymerization depends strongly on the polarity of the solvent, indicating the heterolytic processes are involved in the initiation step.

The effectiveness of cupric acetate as an initiator depends also on the structure of vinylpyridine. 4-VP polymerizes rapidly with the reduction of the cupric species whereas the polymerization of MVP under the same conditions is much slower. Although the reduction of the cupric species by 2-VP is as rapid as that by 4-VP, the polymer of 2-VP is scarcely formed. An example of the reduction of the cupric species as measured by absorption spectroscopy is shown in Figure 5. The absorption of the cupric species at 700 mμ decreases with reaction time.

The sequence of  $R_p$  and the rate of reduction of Cu(II) depending upon the kind of vinylpyridine resembles those of the preceding discussion in that the conjugation between the vinyl group and the metal salt is an important factor for charge transfer. Under the present experimental conditions, cupric acetate in the polymerization system is entirely complexed since the stability constant of pyridine-cupric ion complex is high ( $\log \beta_2 = 4.33$  in water at 25°C where  $\beta_2$  is the overall stability constant of  $CuPy_2^9$ ) and the concentration of Cu(II) is much smaller than that of vinylpyridine. A detailed kinetic study of

polymerization of 4-VP in methanol provides the following kinetic expressions:



$$R_p = f^{1/2} k_d^{1/2} k_p k_t^{-1/2} [\text{complex}]^{1/2} [\text{M}] \quad (11)$$

The concentration of 'complex' depends upon the solvent. In methanol, [complex] is practically equal to the total cupric species and the rate is simply expressed by 12. When 4-VP plus pyridine is kept constant, the

$$R_p = K[\text{Cu(II)}]^{1/2} [\text{M}] \quad (12)$$

cupric species is partitioned between two bases and only the 4-VP-Cu(II) complex takes part in initiation. The rate expression is then given by 13.

$$R_p = K'[\text{Cu(II)}]^{1/2} [\text{M}]^2 \quad (13)$$

The small activation energy of initiation ( $5.4 \times 1.6$  kcal/mol) is further support for electron transfer initiation. The mechanism of initiation would be very similar to the electron transfer reaction between Co(III) and Cr(II) bridge by pyridine carboxylic acid<sup>15</sup>. Cr(II) coordinates to the nitrogen of the pyridine ring and Co(III) is attached to the carboxylate site. The conductivity between Cr(II) and Co(III) is then essential for the electron transfer to proceed via a pyridinecarboxylate bridge. Indeed, the bridged path prevails in pyridine-2-carboxylate and pyridine 4-carboxylate but not in pyridine-3-carboxylate compounds.

Other cupric salts may be used for initiation. However, cupric salts of the ligand transfer type such as cupric halides act as stronger radical terminators. Although cupric halides oxidize vinylpyridine, polymerization is scarcely initiated.

### Polymerization of *N*-vinylcarbazole initiated by cupric salts<sup>16</sup>

Electron transfer initiation should induce both radical and ionic polymerization. With vinylpyridine, cationic polymerization is impossible because of the high basicity of the monomer. However, when cupric salts are supplied to the polymerization of *N*-vinylcarbazole (VCZ) which is very sensitive to cationic initiation, cationic polymerization is exclusively induced. Copolymerization with styrene and additive effects on the rate of polymerization confirm the cationic nature of the polymerization. Although the experimental findings do not necessarily mean electron transfer initiation, initiation mechanisms other than electron transfer are less likely. The action of cupric nitrate as a Friedel-Crafts catalyst or Lewis acid is difficult to accept. The amount of protonic acid which might be produced by the hydrolysis of cupric salt is not sufficient to bring about the observed rate of polymerization as

Table 6. Comparison of polymerization of 4-vinylpyridine (4-VP) with that of *N*-vinylcarbazole (VCZ) initiated by cupric salts<sup>a</sup>

Characteristic	Sequence of $R_p$	
	VCZ	4-VP
$R_p$ in different solvents	Ethylene chloride > tetrahydrofuran > DMF > alcohols, water = 0 (cupric bromide as initiator [ $\text{Cu}^{II}$ ] = $10^{-4} \sim 10^{-2}$ )	Water > acetone > methanol > DMF > benzene, tetrahydrofuran, ethylene chloride 0 (cupric acetate as initiator)
Effect of cupric salts	$\text{CuBr}_2 > \text{CuCl}_2 \approx \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} > \text{Cu}(\text{CH}_3\text{COO})_2$ (pyridine) = 0 (in tetrahydrofuran and in DMF [ $\text{Cu}^{II}$ ] = $10^{-1} \sim 10^{-2}$ mole/l.)	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O} > \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} > \text{CuBr}_2$ , $\text{CuCl}_2 \approx 0$ (in methanol [ $\text{Cu}^{II}$ ] = $1.0 \times 10^{-2}$ mole/l.)
Effect of oxygen	Retardation	Inhibition

<sup>a</sup> Reaction conditions: VCZ, [monomer] = 0.7 mole/l., polymerization at 30°C for 3 h, 4-VP, monomer/solvent = 1/1 by volume, polymerization at 50°C for 2.5 h.

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confirmed by reference experiments. The polymerization of VCZ can also be induced by other oxidizing metal salts such as those of Fe(III) and Ce(IV). A comparison of the polymerization of VCZ with that of 4-VP is shown in Table 6. The preference of solvent and anion is markedly different between NCZ and 4-VP. It is understandable that cationic polymerization favours ethylene chloride to water as solvent and halides to acetate as a counter anion. Cupric nitrate is an effective initiator for both cationic and radical polymerization. This is a good example that a single initiator can act in both these ways.

### Photopolymerization of *N*-vinylimidazole sensitized by oxidizing metal salts<sup>8</sup>

*N*-Vinylimidazole resembles VCZ in the sense that both monomers are *N*-vinyl compounds. On the other hand, *N*-vinylimidazole contains a very

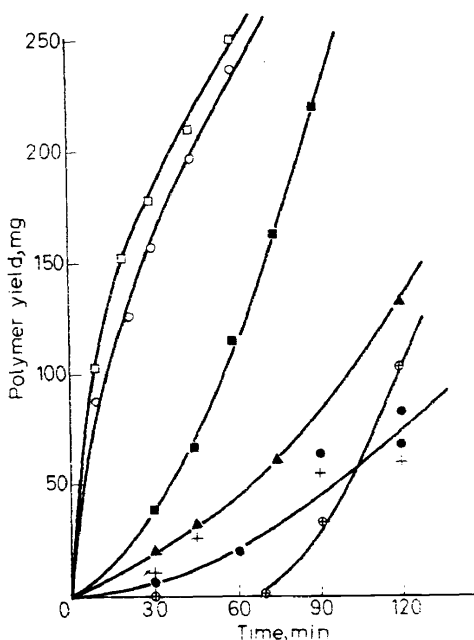


Figure 6. Photopolymerization of 2-ethyl-1-vinylimidazole at 30°C: monomer 1.5 ml, [metal salt] =  $10^{-3}$  M in vacuo. ●: no metal salt, ▲: AgNO<sub>3</sub>, ■: Hg(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, ○: Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>, □: UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ⊕: Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, ⊕: NaAuCl<sub>4</sub>·2H<sub>2</sub>O.

basic nitrogen as does vinylpyridine. It is a point of interest to examine the behaviour of the metal salt in the initiation process. In contrast to vinylpyridine, oxidizing metal salts do not initiate polymerization thermally. Under photoirradiation by a 300W high pressure mercury lamp, however, certain oxidizing metal salts sensitize the polymerization as shown in Figure 6. The effect of these salts on catalysed radical polymerization is negligible with the exceptions of cupric acetate and sodium chloroaurate which terminate the growing polymer radical. The gold salt is a very strong oxidant and the radical polymerization of styrene is also inhibited by the

gold salt. The large and negative  $e$  value of *N*-vinylimidazole ( $e = -1.61$  for 2-methyl-1-vinylimidazole<sup>10</sup>) indicates ease of oxidation of growing polymer radicals in comparison with 4-VP. Consequently, cupric acetate leads to linear termination in the polymerization of *N*-vinylimidazole but not in that of 4-VP. The finding that only oxidizing metal salts such as those of Ce(IV), U(VI), Hg(II) and Ag(I) are effective sensitizers whereas Zn(II) is inert points strongly to the photosensitized redox initiation of polymerization. The photopolymerization of styrene in acetonitrile is sensitized neither by U(VI) nor by Ce(IV), indicating the importance of specific interaction between metal salt and *N*-vinylimidazole.

### Thermal and photopolymerization of *N*-vinylcarbazole sensitized by sodium chloroaurate<sup>18</sup>

Although sodium chloroaurate ( $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ ) has been known as a very photosensitive salt, its photochemistry is entirely unsurveyed. The polymerization of VCZ in the presence of  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  is greatly photosensitized as shown in Figure 7 whereas thermal polymerization in the dark starts after an induction period<sup>19</sup>. The action of the gold salt as an initiator can very likely be correlated to its oxidizing property. Such negatively charged species as  $\text{AuCl}_4^-$  would not be Friedel-Crafts catalysts which initiate cationic polymerization without redox processes.

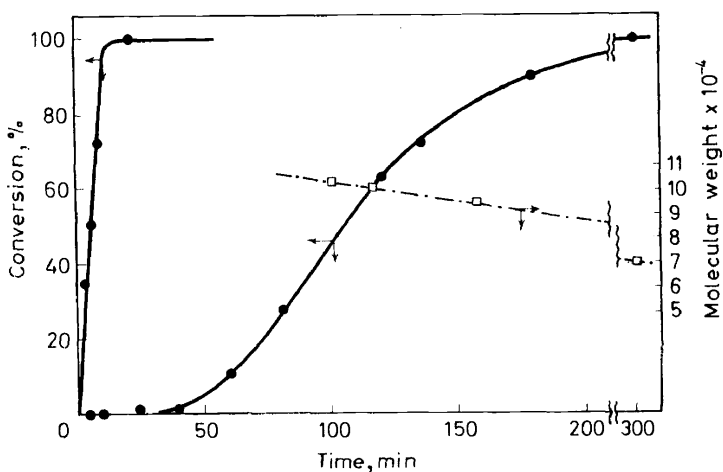


Figure 7. Effect of photoirradiation on the polymerization of VCZ initiated by  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  at 30°C in air. Solvent: nitrobenzene.  $[\text{VCZ}] = 0.25\text{M}$ ,  $[\text{Au}^{\text{III}}] = 1.0 \times 10^{-4}\text{M}$ . (1) ● time/conversion, polymerization in the dark; (2) ○ time/conversion, a hard glass, cylindrical polymerization vessel was irradiated by the mercury lamp from a distance of 28 cm. (3) □ polymerization time/molecular weight, polymerization in the dark.

The additive effects shown in Table 7 are pieces of confirmatory evidence for the cationic nature of the propagation and also for the fact that redox processes must play important roles in the initiation step. The inhibitory

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effect of ammonia, the retardation of polymerization and the decreased molecular weight in the presence of water and also efficient propagation in the presence of DPPH confirm the cationic propagation. In addition, the solvent is nitrobenzene which is one of the most unfavourable solvents for

 Table 7. Polymerization of VCZ in the presence of various additives<sup>a</sup>

Additive	Polymn time, min	Convsn, %	Average mol. wt
None (standard)	120	67.5 ± 5	98000
Ammonia, 10 <sup>-2</sup> to 10 <sup>-3</sup> M	120	0	
Water, 10 <sup>-2</sup> M	160	~90	66000
Water, 10 <sup>-1</sup> M	180	~90	35000
N-Ethylcarbazole, 0.125M	80	50	94000
N-Ethylcarbazole, 0.25M	90	50	90000
Ascorbic acid <sup>b</sup>	120	100	
Mercury metal <sup>b</sup>	120	100	
Ferrocene, 5 × 10 <sup>-5</sup> M	30	100	
DPPH, 10 <sup>-4</sup> M	90	96	

<sup>a</sup> [VCZ] = 0.25M, [NaAuCl<sub>4</sub>·2H<sub>2</sub>O] = 1.0 × 10<sup>-4</sup> M; solvents, nitrobenzene, 30°C.

<sup>b</sup> Additive is insoluble.

radical polymerization. Acceleration of polymerization by reducing agents such as ascorbic acid, mercury and ferrocene would suggest the gold in its intermediate valency state is an effective initiator. Standard redox potentials of relevant redox pairs are presented in Table 8. An important point derived

Table 8. Standard redox potentials of relevant compounds

Redox pair	E°, V	Determination
AuCl <sub>4</sub> <sup>-</sup> /AuCl <sup>II</sup>	- 0.5 to - 0.96	estimation from redox reaction
Au <sup>III</sup> <sub>Cu</sub> /AuCl <sub>2</sub> <sup>-</sup>	> - 1.4	polarography in DMF estimation
VCZ <sup>+</sup> ·/VCZ	- 1.3	from redox reaction
Ferrocene <sup>+</sup> /ferrocene	+ 0.56	polarography in DMF
Hg <sub>2</sub> <sup>2+</sup> /Hg(l)	- 0.792	e.m.f. in alcohol
Ascorbic acid	+ 0.1 to + 0.3	e.m.f.

from Table 8 is that Au(II) is a much stronger oxidant than Au(III) and a rapid electron transfer process is energetically possible between VCZ and Au(II) but not between VCZ and Au(III). Reducing agents which accelerate the polymerization are all strong enough to reduce Au(III) to Au(II). Consequently, a reasonable interpretation of the initiation mechanism is the preliminary reduction of Au(III) to Au(II) by reducing agents and then the Au(II) species initiates polymerization most probably by an electron transfer oxidation of the monomer. In support of this view, a clear singlet e.s.r. signal is observed in the polymerization system. The singlet spectrum in Figure 8

would be attributed to the free spin delocalized over the carbazyl group. Along the same line of discussion, the induction period in the absence of reducing agents is interpreted as the time required to accumulate Au(II) by a

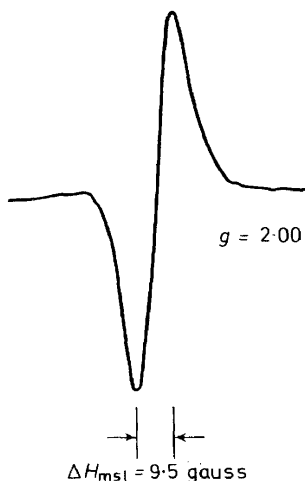
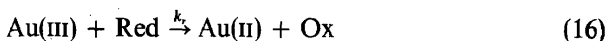
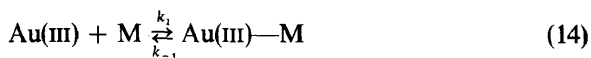


Figure 8. Electron spin resonance spectrum of VCZ-NaAuCl<sub>4</sub>·2H<sub>2</sub>O-nitrobenzene system, made at 77°K after reaction at room temperature; [VCZ] = 0.5M and [Au<sup>III</sup>] = 7.5 × 10<sup>-3</sup>M.

slow reaction between Au(III) and VCZ. The kinetic study of the induction period supports the interpretation mentioned above. The following kinetic scheme explains the total polymerization behaviour.

Initial process:



(in the presence of reducing agents)

Initiation:



Propagation:



Termination:



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The rate expressions based on a stationary state assumption are given by equation 21 for polymerization after the induction period in the absence of reducing agents and by equation 22 for polymerization in the presence of reducing agents, i.e. under the condition that the Au(II) is produced exclusively by reaction 16. These rate expressions agree well with experimental data.

$$-d[M]/dt = [k_1 k_2 k_p / k_t (k_2 + k_{-1})] [Au(III)] [M] \quad (21)$$

$$-d[M]/dt = (k_p k_r / k_t) [Au(III)] [Red] \quad (22)$$

Table 9. Dependence of  $R_p$  on the wavelength of irradiation

Wavelength of irradiation m $\mu$	Incident intensity, 10 <sup>-10</sup> E.min <sup>-1</sup> .cm <sup>2</sup>	$R_p$ (10 <sup>-5</sup> mole <sup>-1</sup> .min <sup>-1</sup> )
548	~1000	<30
437	895	1300
365	682	420
313	89.6	320
254	~8	<20

The effect of photoirradiation would be to produce active Au(II) species<sup>19,20</sup>. It is always a difficult problem in photochemistry to decide the energy absorbing species when the absorption spectra of several species overlap. The absorption spectra of relevant species are shown in Figure 9. The photoirradiation at 437 m $\mu$  is absorbed by the nitrobenzene-VCZ complex, nitrobenzene and Au(III) (also by the polyVCZ-nitrobenzene complex after the formation of polyVCZ). Under the polymerization conditions ([VCZ] = 0.25M, [Au(III)] = 10<sup>-4</sup> ~ 10<sup>-5</sup>M in nitrobenzene), almost all the photoenergy is absorbed by the nitrobenzene-VCZ complex and nitrobenzene

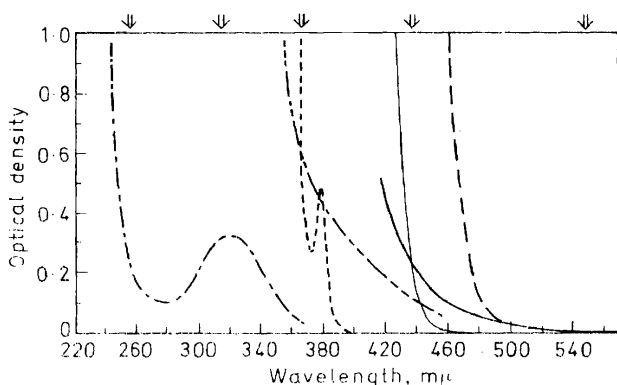


Figure 9. Electronic spectra of relevant compounds: —: [Au<sup>III</sup>] = 2 × 10<sup>-3</sup>M in nitrobenzene (absorption of nitrobenzene is subtracted); - - - -: [Au<sup>III</sup>] = 6 × 10<sup>-3</sup>M in methanol; - · - · - ·: [Au<sup>III</sup>] = 1.2 × 10<sup>-3</sup>M in methanol; - - - - -: [VCZ] = 0.25M in nitrobenzene; - - - - -: [VCZ] = 0.25M in benzene; —: nitrobenzene.

itself and an extremely small fraction of energy is taken up by the Au(III) species. Kinetic study of the photopolymerization indicates that the photoenergy absorbed by the Au(III) species alone is utilized to initiate polymerization. The quantum yield of monomer consumption based on the photoenergy absorbed by the Au(III) species is about  $10^7$ . This figure is surprisingly high in comparison with the known figures of photopolymerization by radical mechanisms. Although the growing cation of polyVCZ is terminated by the monomer which is susceptible to electrophilic attack at the carbazyl group as well as at the vinyl group, the termination process of cationic polymerization is, in general, not as efficient as that of radical polymerization. Consequently, there is a good possibility of developing very fast photochemical reactions by the application of photosensitized redox reactions which can initiate cationic chain reactions.

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