

# Complexes of 1-Vinylazoles with Transition Metals in Radical Polymerization

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**ABSTRACT:** Radical polymerization of the complexes of 1-vinylimidazole, 1-vinylbenzimidazole, and 1-vinylbenztriazole with  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{ZnCl}_2$  was investigated. It was found that the polymerization is accompanied by spontaneous polymerization in the case of  $\text{MnCl}_2$  and  $\text{ZnCl}_2$ , inhibition by coordination of macroradicals with  $\text{Ni}^{2+}$  ions, and a gel effect by crosslinking of the formed polymer during the complexing with  $\text{Zn}^{2+}$ . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 101–108, 2000

**Key words:** polymerization; azole; vinyl; metal; complex

## INTRODUCTION

Polymerization of metal-containing monomers is a convenient method for the synthesis of new polymers with useful properties: catalysts, biological active preparations, etc.<sup>1–3</sup> The mechanism of the radical polymerization in these systems has some peculiarities, which are connected with the nature of the metal, unsaturated ligands, and solvent. We discuss here the results of investigations of the polymerization of some *N*-vinylazole (VAZ) complexes with transition-metal chlorides— $\text{MnCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{ZnCl}_2$ . We used 1-vinylimidazole (VI), 1-vinylbenzimidazole (VBI), and 1-vinylbenztriazole (VBT) as vinylazoles, which are bases with rather different basicities (Table I). The chosen metals differ by the electron structure of their cations, so in the case of  $\text{Mn}^{2+}$ , the half-filled *d*-shell leads to its reducing properties, which considerably decrease for  $\text{Ni}^{2+}$  (*d*<sup>8</sup>), whereas the  $\text{Zn}^{2+}$  with the completely filled *d*-shell is inactive in red-ox processes.

## EXPERIMENTAL AND CALCULATIONS

VI (bp 346 K/0.93 kPa,  $n_D^{20}$  1.5310) and VBI (bp 398 K/0.40 kPa,  $n_D^{20}$  1.6260) were obtained by the reaction of imidazole or benzimidazole with acetylene<sup>5</sup>; VBT (bp 371 K/0.166 kPa,  $n_D^{20}$  1.6100) was synthesized by interaction of benztriazole with vinyl acetate.<sup>6</sup> The complexes were prepared by the mixing of VAZ and metal chlorides in ethanol at 298 K in a 2 : 1 ratio followed by filtration and washing of the precipitates with ethanol (Table II).

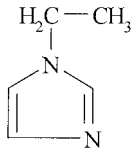
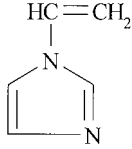
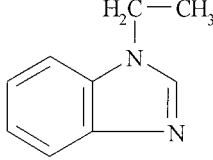
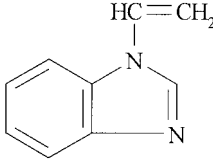
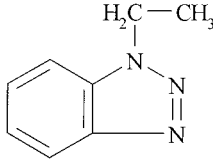
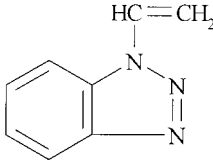
Azobisisobutyronitrile (AIBN)-initiated and spontaneous polymerization of the complexes was conducted in dimethylformamide (DMF) in evacuated ampules. Polymers were isolated by precipitation into ethanol, washed with a precipitating agent, and dried in a vacuum to a constant weight. The content of  $\text{MeCl}_2$  (Me is Mn, Ni, or Zn) in monomeric and polymeric complex compounds was determined from the data of elemental analysis for Cl. Detailed conditions and results of polymerization are summarized in Table III. The radical character of polymerization was confirmed by inhibition of the process with *p*-benzoquinone and 1-oxy-2,2,6,6-tetramethylpiperidine.

The kinetics of polymerization was studied by gravimetry (VI complexes), dilatometry (VBI com-

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**Table I Basicity ( $pK_a$ ) of Vinylazoles and Their Ethyl Derivatives<sup>4</sup>**

Substance		$pK_a$
1-Ethylimidazole		8.87
1-Vinylimidazole (VI)		7.32
1-Ethylbenzimidazole		7.49
1-Vinylbenzimidazole (VBI)		5.64
1-Ethylbenztriazole		3.49
1-Vinylbenztriazole (VBT)		2.00

plexes), and spectrophotometry (VBI and VBT complexes). In the case of gravimetry, weighing of the precipitates was done. For VBI complexes, the contraction coefficients ( $C_C$ ) were calculated as the difference between specific volumes of the monomer and polymer and were verified by comparison with the data of gravimetry at 333 K (Table IV). Yield of the polymers ( $A$ , %) was calculated as

$$A = \frac{\Delta V \times 100}{VC_c}$$

where  $V$  is the initial volume of the monomer, and  $\Delta V$ , the change of the reaction mixture volume.

Spectrophotometry investigations were based on the absorption bands of vinyl groups of VBI and VBT in DMF at 295 and 303 nm, respectively. Comparability of the methods was confirmed by gravimetric analysis at some points of the kinetics curves for all the systems. Orders of the polymerization reactions were obtained from the linear dependence between  $\lg(w)$  and  $[I]$  or  $[M]$  at  $[M] = 1$ ,  $[I] = 0.001\text{--}0.009$  mol/L (initiator order) and at  $[I] = 0.01$ ,  $[M] = 0.25\text{--}2$  mol/L (monomer order). Details of the experiments were discussed earlier.<sup>7-9</sup>

Polarographic investigations were carried out in a cell with a Hg-dropping electrode in DMF in the presence of 0.1N tetramethylammonium perchlorate as a background electrolyte, in argon.

**Table II Complexes of Vinylazoles and Metal Chlorides**

Complex	Yield (%)	Melting Point (K)	Color	Solubility	Cl (%), Elemental Analysis	
					Found	Calculated
2VI · ZnCl <sub>2</sub>	90	411–412	White	DMF, DMSO*, H <sub>2</sub> O	22.1	21.9
2VI · MnCl <sub>2</sub>	95	>513	White–pink	DMF, DMSO*, H <sub>2</sub> O	23.2	22.6
2VI · NiCl <sub>2</sub>	80	475–476	Blue	Hot DMF	14.3	14.0
2VI · SnCl <sub>2</sub>	70	534–535	White	Hot DMF	31.5	31.1
2VBI · ZnCl <sub>2</sub>	85	468–469	White	DMF, H <sub>2</sub> O	16.8	16.5
2VBI · MnCl <sub>2</sub>	90	509	Pink	DMF, H <sub>2</sub> O-ethanol (1 : 1)	16.6	17.1
2VBI · NiCl <sub>2</sub>	70	493–495	Green	DMF, DMSO	16.5	17.0
2VBI · SnCl <sub>2</sub>	65	553–554	White	DMF, DMSO	25.8	25.8
2VBT · ZnCl <sub>2</sub>	80	493–494	White	DMF, H <sub>2</sub> O	16.6	16.3
2VBT · MnCl <sub>2</sub>	80	412	Pink	DMF, H <sub>2</sub> O-ethanol (1 : 1)	25.9	26.2
2VBT · NiCl <sub>2</sub>	60	483–484	Yellow–green	DMF	16.8	16.9
2VBT · SnCl <sub>2</sub>	50	518–521	White	DMF	25.9	25.8

The half-wave potential  $E_{1/2}$  was  $-0.33$  V for NiCl<sub>2</sub> and  $-0.435$  V for ZnCl<sub>2</sub>. The stability constants ( $K_C$ ) and the number of ligands ( $P$ ) were calculated from the polarographic wave equation:

$$(E_{1/2})_C - (E_{1/2}) = \frac{1}{n} \ln K_C - \frac{P}{n} \ln C_L$$

where  $(E_{1/2})_C$  is the half-wave potential of the complex;  $n$ , the number of electrons in the reduction process (two in all systems); and  $C_L$ , the ligand concentration. In the case of MnCl<sub>2</sub>, the

**Table III Polymerization of the Coordinated Vinylazoles**

Monomer	Conversion (%)	Composition of the Polymeric Complex	
		Cl (%) Elemental Analysis	VAZ : MeCl <sub>2</sub>
2VI · ZnCl <sub>2</sub> <sup>a</sup>	64.8	20.7	2.2 : 1
2VBI · ZnCl <sub>2</sub> <sup>a</sup>	21.6	14.2	2.5 : 1
2VBT · ZnCl <sub>2</sub>	6.9	8.1	5 : 1
2VI · MnCl <sub>2</sub>	77.0	19.7	2.5 : 1
2VBI · MnCl <sub>2</sub>	37.8	8.3	5 : 1
2VBT · MnCl <sub>2</sub>	6.5	8.2	5 : 1
2VI · NiCl <sub>2</sub>	28.5	20.5	2.3 : 1
2VBI · NiCl <sub>2</sub>	14.0	13.3	2.8 : 1
2VBT · NiCl <sub>2</sub>	7.1	8.2	5 : 1

DMF,  $[M] = 0.5$  mol/L,  $[I] = 0.02$  mol/L, 333 K, time 3 h.

<sup>a</sup> Time = 0.5 h.

polarographic wave is usually not observed in DMF solutions.<sup>10</sup>

The polymerization degree of poly-VBI · NiCl<sub>2</sub> was evaluated by viscometry (propyl alcohol, 293 K,  $\alpha = 0.70$ ,  $K = 0.75 \times 10^{-4}$ ; ref. 11) after desorption of NiCl<sub>2</sub>. Desorption of NiCl<sub>2</sub> was carried out by dissolving the polymer in 0.1N HCl with subsequent alkalifying of the solution by NH<sub>4</sub>OH. The precipitated poly-VBI was filtrated, washed by water, and reprecipitated from ethanol into water.

Quantum-chemical calculations were performed using the HyperChem 3.0 program by the ZINDO/1 method<sup>12</sup> with full geometry optimization. When considering the coordination compounds, we used a single molecule of VAZ and three to five molecules of the solvent as ligands, because complexes of metal chlorides with VAZ are considerably ionized in DMF.<sup>13</sup> Coordination numbers were 6 for Mn<sup>2+</sup> and Ni<sup>2+</sup> and 4 for Zn<sup>2+</sup>, according to ref. 14. DMF molecules were replaced by formamide to facilitate the calculations.

**Table IV Specific Volumes and Contraction Coefficients of VBI Complexes**

Monomer	Specific Volumes		Contraction Coefficients
	Monomer	Polymer	
2VBI · ZnCl <sub>2</sub>	0.674036	0.580736	0.0933
2VBI · MnCl <sub>2</sub>	0.680272	0.493972	0.1863
2VBI · NiCl <sub>2</sub>	0.699252	0.637252	0.062

**Table V** Stability Constants of Vinylazole Complexes with Metal Chlorides

Complex	lg $K$
VI · NiCl <sub>2</sub>	0.539
VBI · NiCl <sub>2</sub>	-0.414
VI · ZnCl <sub>2</sub>	0.565
2VI · ZnCl <sub>2</sub>	-0.765
VBI · ZnCl <sub>2</sub>	-1.104
VBI · MnCl <sub>2</sub>	-2.63

## RESULTS AND DISCUSSION

Interaction of VAZ with metal chlorides in ethanol gives rise to crystalline complexes with the composition MeCl<sub>2</sub> : ligand = 1 : 2, which are soluble only in electron-donating solvents such as DMF. Dissolution of the complexes is accompanied by their stepwise dissociation, the degree of which depends on the basicity of the VAZ. Stability constants of the VI and VBI complexes were determined using polarographic reduction (Table V) and they point to a greater stability of the complexes with VI. No shift of the reduction wave was found in systems with VBT that points to the full dissociation of these complexes.

Polymerization of the coordinated VAZ in DMF under the action of AIBN leads to polymers which contain less metal chloride than do the starting complexes depending on their stability (Table III). IR spectra of the polymers contain characteristic bands of the azole groups (1520, 1110, 940–960 cm<sup>-1</sup>, imidazole groups; 1500, 1290, 900 cm<sup>-1</sup>, benzimidazole groups; and 1490, 1230, 1100 cm<sup>-1</sup>, benztriazole groups) and do not contain absorption bands of the vinyl groups of VAZ (1640, 990 cm<sup>-1</sup>).

### Polymerization of MnCl<sub>2</sub> Complexes

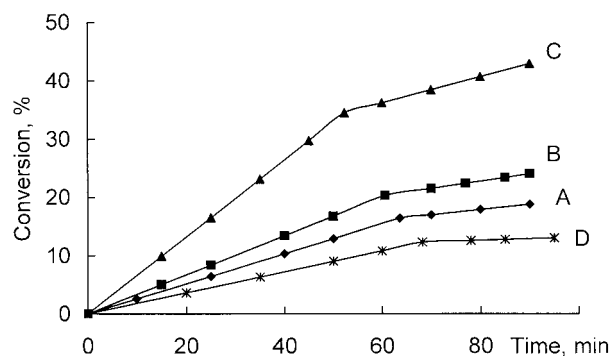
When polymerizing MnCl<sub>2</sub> complexes with VBI and VBT under the action of AIBN, we observed an increase of the initial rate of the reaction as compared with free monomers and the polymerization rate sharply decreases at 15–30% conversion (Fig. 1). The general kinetic equation for polymerization of 2VBI · MnCl<sub>2</sub> was derived as  $w = [M][I]^{0.34}$ . The obtained value of the reaction order toward the initiator may be a result of the spontaneous polymerization (*SP*) of the coordinated monomer. Our efforts to investigate the kinetics of *SP* of 2VBI · MnCl<sub>2</sub> were unsuccessful

because of poor reproducibility of the experimental data. It seems likely that the *SP* in this system is connected with the presence of a small amount of an initiator in the system, after the exhausting of which the reaction is finished. Mn<sup>3+</sup> ions may act as this initiator since they may be formed by oxidation of Mn<sup>2+</sup> by oxygen of the air during preparation of the working solutions and the ability of Mn<sup>3+</sup> to act as a component of the red-ox initiating systems involving nitrogen-containing substances is known.<sup>3</sup> This conclusion is supported by an increase of the *SP* rate after preliminary saturating of the reaction medium with oxygen and by an absence of *SP* when the monomer solution was prepared in a vacuum with a preliminary degassed solvent. The presence of catalytic amounts of Mn<sup>3+</sup> in solutions of the complex leads to a small wave of polarographic reduction at -0.77 V.

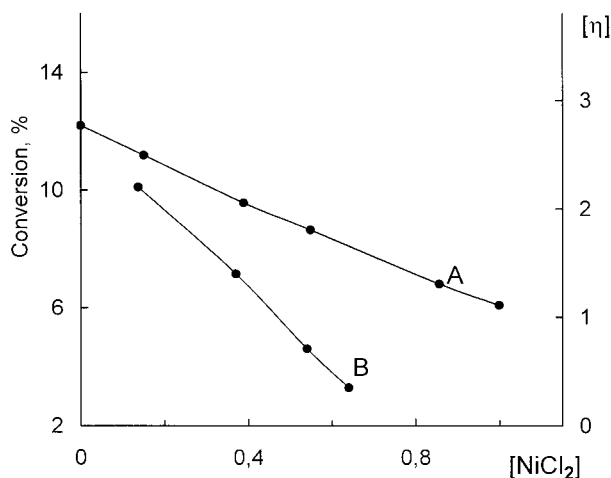
The electron-donating solvent (DMF) is necessary for *SP* in systems with MnCl<sub>2</sub>, since this reaction was not observed in ethanol solutions of 2VBI · MnCl<sub>2</sub>, whereas the addition of MnCl<sub>2</sub> (0.01 mol/L) increased the rate of thermoinitiated polymerization of styrene in DMF by about 20 times. Influence of DMF on the oxidation ability of Mn<sup>2+</sup> ions is confirmed by quantum-chemical calculations of six-coordinated complexes of Mn<sup>2+</sup> and Mn<sup>3+</sup> with water and formamide in which the oxidation enthalpy is lower by 135 kcal/mol than in water.

### Polymerization of NiCl<sub>2</sub> Complexes

In the case of VAZ complexes with NiCl<sub>2</sub>, we observed a decrease of the AIBN-initiated polymerization rate as compared to free VAZ, except



**Figure 1** Polymerization of 2VAZ · MnCl<sub>2</sub> (1 mol/L, 333 K). [AIBN]: (A) 0.004; (B) 0.01; (C,D) 0.02. (A–C) VAZ–VBI; (D) VBT.



**Figure 2** Dependence of (A) VBI conversion and (B) intrinsic viscosity of poly-VBI in DMF from  $\text{NiCl}_2$  concentration.

for the  $2\text{VBT} \cdot \text{NiCl}_2$  system, which is fully dissociated in DMF. The reaction order toward the initiator is 0.5 for  $2\text{VBI} \cdot \text{NiCl}_2$ , whereas the dependence of  $\lg(w)$  on  $\lg[M]$  is nonlinear and the reaction order relative to the monomer decreases from 1 to 0.7 as the monomer concentration increases from 0.2–0.47 mol/L to 0.34–0.9 mol/L. The polymerization degree of poly-VBI, which was obtained from  $2\text{VBI} \cdot \text{NiCl}_2$  at  $[\text{AIBN}] = 0.009\text{M}$  and  $[\text{M}] = 0.25\text{--}0.7\text{M}$ , is 70–140, which is significantly lower than is the polymerization degree of free VBI (250–790). Polymerization in the presence of various concentrations of  $\text{NiCl}_2$  at constant VBI concentration (Fig. 2) shows a decrease of the polymerization rate and molecular mass of poly-VBI with increase of the salt concentration.

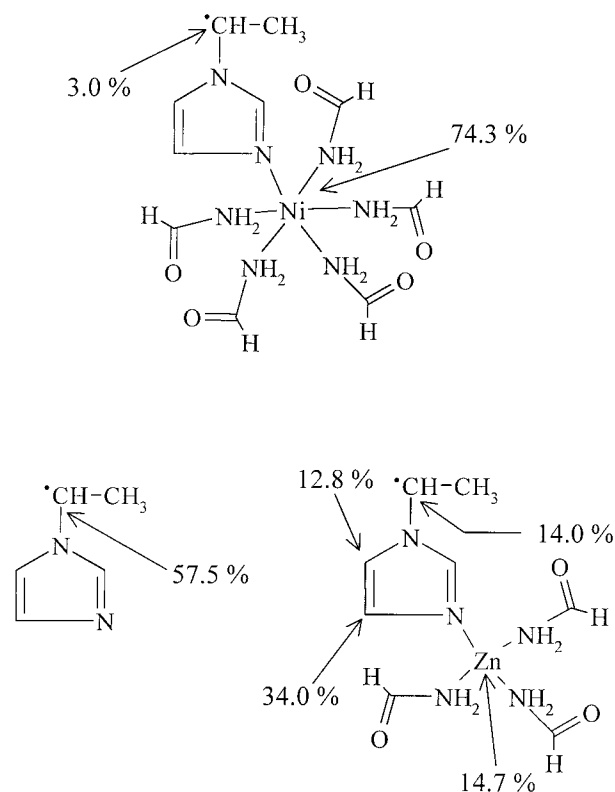
The results obtained may be associated with a soft inhibiting action of  $2\text{VBI} \cdot \text{NiCl}_2$  on the radical polymerization. The participation of the VBI complexes with  $\text{NiCl}_2$  in inhibition instead of the free  $\text{Ni}^{2+}$  ions is confirmed by invariability of the polymerization rate of styrene with addition of  $\text{NiCl}_2$ . The probable mechanism of the inactivation of the growing macroradical in coordination with  $\text{NiCl}_2$  may be due to delocalization of the noncoupled electron with the  $\text{Ni}^{2+}$  ion that has an unfilled  $d$ -level.

To verify this assumption, we made quantum-chemical calculations of the structures simulating the complexes of the growing macroradicals. The results (Fig. 3) show a significant localization of the noncoupled electron at the metal ion in the case of the  $\text{Ni}^{2+}$  complex in contrast to the free

macroradical and the  $\text{Zn}^{2+}$  complex. We found that for the radical coordinated with  $\text{Mn}^{2+}$ , which has an odd number of electrons, the system has no noncoupled electrons in the basic state and the difference between energies of the lowest vacant molecular orbital and the highest occupied molecular orbital is rather high (0.3 eV), which excludes their degeneration. So, the coordination with  $\text{Mn}^{2+}$  also has to inactivate the radical, but this effect does not reveal itself in the kinetic experiments because of a prevalence of the additional redox initiation.

### Polymerization of $\text{ZnCl}_2$ Complexes

In investigating the polymerization kinetics of  $\text{Zn}^{2+}$  complexes, we determined the initial polymerization rates, the reaction orders toward the monomer and initiator, and the activation energy of the polymerization (Table VI). The high reaction order toward the initiator ( $>0.5$ ) may result from the monomolecular mechanism of the chain termination such as in the polymerization of 1-vinyl-1,2,4-triazole.<sup>15</sup> The increase of the polymerization rates of  $2\text{VI} \cdot \text{ZnCl}_2$  and  $2\text{VBI} \cdot \text{ZnCl}_2$  (Fig.



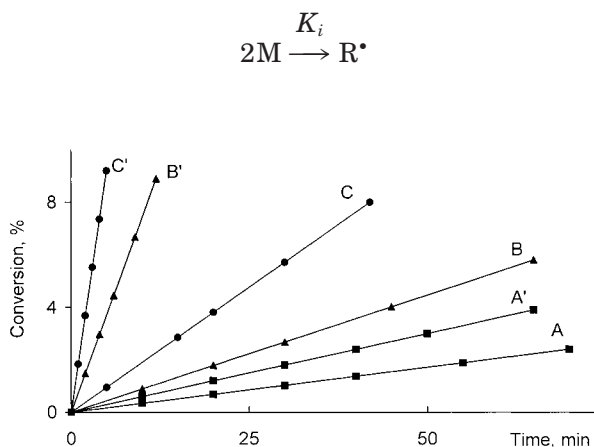
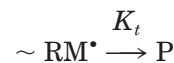
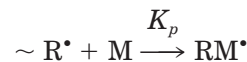
**Figure 3** Localization of the noncoupled electron in radicals simulating the growing macroradicals.

**Table VI Kinetic Parameters of the Radical Polymerization of Vinylazoles Complexes with ZnCl<sub>2</sub> (DMF)**

Monomer	Reaction Orders (333 K)			$E_a$ (kcal/mol)
	Monomer	Initiator		
2VI · ZnCl <sub>2</sub>	1.2	0.7		20.2
2VBI · ZnCl <sub>2</sub>	1.0	1.0		17.0
2VBT · ZnCl <sub>2</sub>	2.0	0.8		13.2

4) in comparison with the free monomers is attributable to an increase of the electron-acceptor properties of the substituent at the double bond in coordination with ZnCl<sub>2</sub>. In the case of 2VBT · ZnCl<sub>2</sub>, which is nearly fully dissociated in solution, the increase of the polymerization rate is due to *SP*, the rate of which is comparable to the rate of the polymerization under the action of AIBN. So, the rate of *SP* is equal to  $2.8 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$  at  $[M] = 1 \text{ mol/L}$ , and in the presence of 0.01 mol/L AIBN, the rate is  $4.0 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ . The larger influence of *SP* on the polymerization of 2VBT · ZnCl<sub>2</sub> leads to a decrease of activation energy of the polymerization (Table IV). *SP* is observed also for the complexes of VI and VBI, but its rate is much lower than the AIBN-initiated polymerization rate.

*SP* of the zinc complexes was investigated with 2VBI · ZnCl<sub>2</sub>. The reaction order of *SP* toward the monomer is 2.8, which agrees with the kinetic scheme, suggesting participation of two monomer molecules in the chain initiation and the monomolecular chain termination:

**Figure 4** Polymerization of VAZ: (A) VBT; (B) VBI; (C) VI and (A', B', C') their complexes with ZnCl<sub>2</sub>. [VAZ], 0.5 mol/L; [AIBN], 0.02 mol/L.

The polymerization rate is expressed as

$$W = K_p [RM^*] [M] \quad (1)$$

The steady-state assumption leads to

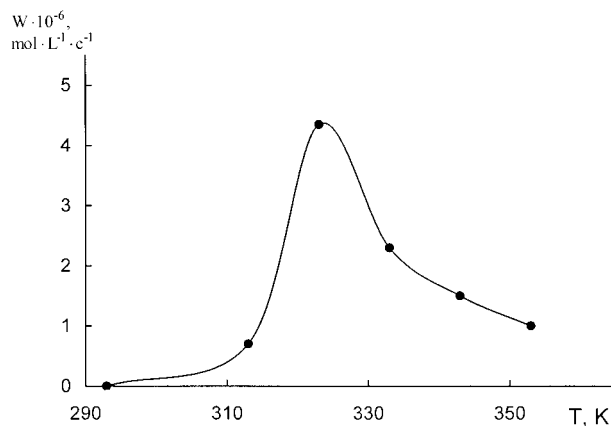
$$K_i [RM^*] = K_t [M]^2 \quad (2)$$

considering monomolecular termination. Combining (1) and (2), we have

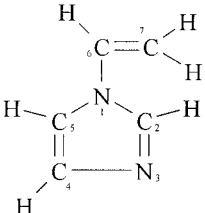
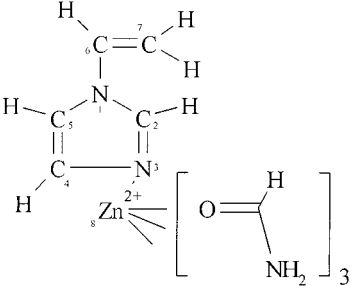
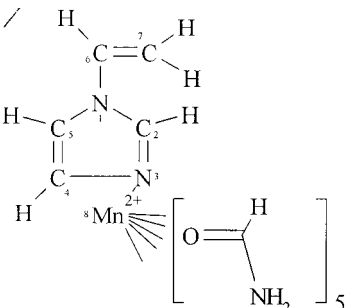
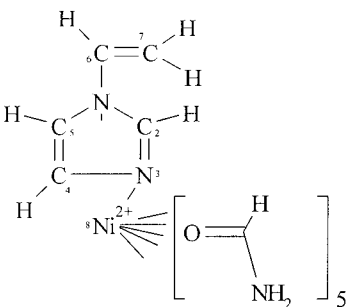
$$[RM^*] = \frac{K_i}{K_t} [M]^2 \quad (3)$$

$$W = \frac{K_i}{K_t} K_p [M]^3$$

Taking into consideration that the noncoordinated monomer has no tendency to *SP*, we may suggest that the coordinated molecules of VAZ participate in the stage of initiation. This suggestion is supported by the temperature dependence of the rate of *SP* (Fig. 5) that has the form of a curve with a maximum. The decrease of the rate at high temperatures may have re-

**Figure 5** Temperature dependence of the spontaneous polymerization rate of 2VBI · ZnCl<sub>2</sub> ( $[M] = 1 \text{ mol/L}$ ).

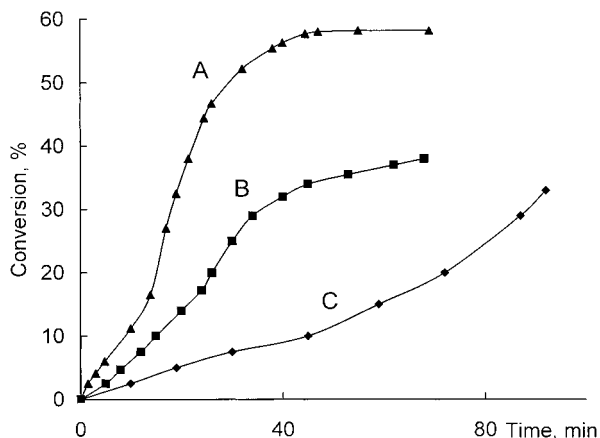
**Table VII Quantum-chemical Calculations of VAZ Complexes**

Substance	Charges		Bond Orders			
	$C_\alpha$	$C_\beta$	Bond	Order	Bond	Order
	0.082	-0.195	1-2	1.194	2-3	1.642
			3-4	1.185	4-5	1.705
			5-1	1.111	1-6	1.034
			6-7	1.953		
	0.131	-0.130	1-2	0.949	2-3	0.970
			3-4	0.921	4-5	1.015
			5-1	0.924	1-6	0.969
			6-7	1.961	8-3	0.009
			8-2	0.035	8-1	0.119
			8-5	0.829	8-4	0.039
			8-6	0.261	8-7	0.016
	0.053	-0.127	1-2	1.357	2-3	1.452
			3-4	1.139	4-5	1.719
			5-1	1.124	1-6	0.975
			6-7	1.981	8-3	0.749
			8-2	0.018	8-1	0.016
			8-5	0.009	8-4	0.021
			8-6	0.001	8-7	0.001
	0.072	-0.162	1-2	0.961	2-3	0.950
			3-4	0.939	4-5	1.777
			5-1	1.005	1-6	0.960
			6-7	1.985	8-3	0.319
			8-2	0.013	8-1	0.010
			8-5	0.066	8-4	0.173
			8-6	0.001	8-7	0.001

sulted from an increase of the complex dissociation.

As is known,<sup>4</sup> one of the possible mechanisms of bimolecular autoinitiation is the formation of

biradicals in the reaction by  $C_\beta$  atoms of the monomers. Quantum-chemical calculations were performed to elucidate the influence of the coordination on this reaction (Table VII). Polarization



**Figure 6** Polymerization of (A,B) 2VBI · ZnCl<sub>2</sub> and (C) 2VBT · ZnCl<sub>2</sub> up to high conversions. (A) [M], 0.9, and (B,C) 0.5 mol/L; (A,B) [AIBN], 0.036, and (C) 0.05 mol/L.

of the vinyl group does not significantly change from the free VI to its complexes, but in the case of Zn<sup>2+</sup> complexes, unlike the Mn<sup>2+</sup> and Ni<sup>2+</sup> systems, the metal ion interacts with the  $\pi$ -system of VI. This is reflected in the nonzero bond orders between the metal and atoms of the heterocycle and in the decrease of the orders of multiple bonds to 1. C <sub>$\alpha$</sub>  atoms of the vinyl group are also included in the conjugation with Zn<sup>2+</sup>. Such interactions have to increase the stability of the biradicals by resonance stabilization with the participation of Zn<sup>2+</sup> ions. Polymerization of the VAZ complexes with ZnCl<sub>2</sub> is accompanied by autoacceleration at conversions above 4–14%, which appears to a greater extent in the case of VBI complexes and is less typical for coordinated VBT and is absent for 2VI · ZnCl<sub>2</sub> (Fig. 6).

The more pronounced gel effect during the polymerization of 2VBI · ZnCl<sub>2</sub> may be connected to a different stability of the monomeric and polymeric complexes of VBI with ZnCl<sub>2</sub>. As a result of the significant dissociation of 2VBI · ZnCl<sub>2</sub>, the noncoordinated VBI molecules are mainly polymerized. In this case, the more basic poly-VBI is obtained (Table I), which actively coordinates with Zn<sup>2+</sup>, which leads to crosslinking of the macromolecules and increases the viscosity. In the case of low-basic VBT, the obtaining polymer is low-active in complexing also and the gel effect is

less pronounced. On the other hand, when polymerizing the relatively stable VI complex, Zn<sup>2+</sup> ions are instantaneously coordinated with the polymer chain and they are not active in the interchain crosslinking, which could increase the viscosity of the system.

So, polymerization of the vinylazole complexes with salts of the transition metals is accompanied by SP, inhibition by coordination of macroradicals with metal ion, and the gel effect by crosslinking of the formed polymer during the complexing.

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