Radical Reactions Initiated by Chelate Complexes of Transition Metals. IV.
System Bidentate Ligand—Salt of the Transition Metal—
—Halogen-Containing Compound as Initiator of Vinyl Chloride Polymerization

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The vinyl chloride polymerization initiated by the system of bidentate organic ligand with donor atoms oxygen—nitrogen, nitrogen—nitrogen and oxygen—oxygen in the presence of the salt of the transition metal and halogen-containing compound has been studied. Out of the series of bidentate ligands investigated the derivatives of aminoalcohols are found to be most effective for the vinyl chloride polymerization. The influence of individual metal salts on the rate of vinyl chloride polymerization in the initiation system 1-amino-2-propanol—carbon tetrachloride decreases in the order $Cu(II) \gg Mn(II)$, $Fe(III)$, $Pb(II)$, $Ni(II)$, $Cr(III)$, $Co(II)$, $Zn(II) > Fe(II)$.

Out of the halogen-containing compounds the halogen alkane derivatives polysubstituted on a single carbon, particularly carbon tetrachloride and hexachloroethane are of a most effective influence on the vinyl chloride polymerization in the system 1-amino-2-propanol—salt of a transition metal. For the dependence of polymerization rate R_p on the concentration of 1-amino-2-propanol and copper(II) acetate the equation $R_p = k$ [aminoalcohol]$^{1.85}$[Cu acetate]$^{0.51}$ was obtained.

Initiation systems for the monovinyl polymerization based on the chelate complexes of transition metals were studied by several authors who focused their attention mainly on the chelate complexes of diketones [1, 2], less on those on the basis of aminoalcohols [3]. In a few cases chelate compound was found to be an effective initiator of polymerization only in the presence of a halogen-containing compound [2, 3]. In our preceding papers aimed at the investigation of reaction of chelate complexes with halogen-containing compounds [4] as well as at the application of these systems for the initiation of polymerization of vinyl monomers, we have found that copper(II) chelate of (—)-ephedrine, in the presence of low- or high--molecular halogen-containing compounds initiates the polymerization of vinyl monomers [3, 5]. The use of a low-molecular halogen-containing compound, *e.g.* carbon tetrachloride, chloroform and the like, led to the formation of homopolymer [3], whereas the use of a high-molecular halogen-containing compound, *i.e.* halogen--containing polymer, such as poly(vinyl chloride), chlorinated polypropylene, chlorinated natural rubber and the like, brought about the formation of graft copolymer

of halogen-containing polymer [5]. In further paper [6] we investigated the system aminoalcohol—copper(II) salt—carbon tetrachloride in view of the possible polymerization of vinyl monomers. Such a system represents, as a matter of fact, the system chelate—halogen-containing compound because of the formation of chelate complex in the polymerization system *in situ* owing to the mixing of the ligand with the salt of transition metal. Chelate formation may well be observed visually because of the occurrence of the characteristic blue—blue-violet colouration of the polymerization system. We showed further on [3, 6] that there was no marked difference between the possibility of initiating vinyl monomer polymerization by the system chelate—halogen-containing compound and that by the system aminoalcohol——copper(II) salt—halogen-containing compound. In either of the above-mentioned systems the same initiation mechanism is applicable, what is in both cases suggested *e.g.* by the observed change of the oxidation degree of the transition metal [3, 6]. An analogous initiation system as in paper [6] has lately been used for the initiation of vinyl chloride polymerization [7].

The present paper brings results of the study of vinyl chloride polymerization initiated by the system bidentate ligand with oxygen and nitrogen as donor—salt of transition metal—halogen-containing compound.

Experimental

All of the chemicals used in the work were anal. grade. Vinyl chloride was purified by rectification, its purity, determined chromatographically, being 99.9%. Solution of transition metal salt in aminoalcohol was weighed and introduced into polymerization ampoule and, after bubbling over by argon, the measured amount of vinyl chloride was condensed into the ampoule. Vinyl chloride was measured using a glass calibrated vessel; reading accuracy of volume ± 0.1 ml. The measuring vessel with vinyl chloride was tempered to the temperature of −78°C. After condensing vinyl chloride into polymerization ampoules, the measured amount of halogen-containing compound was metered and the ampoules sealed in nitrogen atmosphere. The sealed ampoules were inserted into a bath annealed to the reaction temperature and, at the end of the polymerization, the ampoules were cooled down by the dry ice—methanol mixture. After opening the ampoules, the unreacted vinyl chloride was degassed. Polymer was extracted by methanol and after decantation, dried in a vacuum drier to constant weight at temperature 60°C and pressure 5 Torr.

Results and Discussion

From the series of the studied bidentate ligands with donor atoms oxygen—oxygen, nitrogen—nitrogen and oxygen—nitrogen respectively, aminoalcohol derivatives are found to be most effective for the polymerization of vinyl chloride (Table 1).

This result is not at all surprising since, in studying the influence of copper(II) chelates on styrene polymerization in the presence of carbon tetrachloride, it was found that copper(II) chelate of (−)-ephedrine, *i.e.* the chelate on the basis of aminoalcohol, is by far more effective for the initiation of styrene polymerization than copper acetylacetonate [3, 9]. Conversion of vinyl chloride is markedly affected by the kind of halogen-containing compound used. The difference consists only in the fact that, in the case of vinyl chloride, we observed more marked differences in the conversions of monomer when individual halogen-containing compounds were used

as components of the initiation system. The rate of vinyl chloride polymerization
was found to be mostly affected by carbon tetrachloride-containing initiation system
used, whereas the concentration of further components of the initiation system
1-amino-2-propanol and copper(II) acetate was constant (Table 2).

Table 1

Influence of the kind of bidentate ligand on vinyl chloride polymerization initiated
by the system ligand—copper(II) acetate—carbon tetrachloride

Vinyl chloride 5 ml, 0.3 ml of copper(II) salt solution in ligand
(0.005 g $Cu(CH_3COO)_2 \cdot H_2O$ in 10 ml of ligand) and 0.3 ml of carbon tetrachloride

Polymerization temperature 30°C, polymerization time 90 minutes

Ligand	Donor atom	VC conversion [%]
ethanolamine	O,N	21.2
diethanolamine		17.2
triethanolamine		15.9
1-amino-2-propanol		24.0
2-diethylaminoethanol		*
ethylenediamine	N,N	2.6
acetylacetone	O,O	0.0
acetylacetone +	O,O	
1-amino-2-propanol	O,N	0.8
(1 : 1 vol.)		

*Traces of polymer.

Table 2

Influence of the type of halogen-containing compound on vinyl chloride polymerization
initiated by the system 1-amino-2-propanol—copper(II) acetate—halogen-containing
compound

Vinyl chloride 5 ml, 0.3 ml of copper(II) salt solution in 1-amino-2-propanol
(0.005 g $Cu(CH_3COO)_2 \cdot H_2O$ in 10 ml of 1-amino-2-propanol), 0.3 ml of halogen-con-
taining compound

Polymerization temperature 30°C, duration of polymerization 90 minutes

| Halogen-containing compound	VC conversion [%]
carbon tetrachloride	24.0
hexachloroethane*	8.4
dibromoethane	**
chloroform	**
methylenechloride	0.0
—	0.0

* 0.3 g.
** Traces of polymer.

Out of the series of salts of transition metals copper(II) salts are found to be of greatest influence on the rate of vinyl chloride polymerization (Table 3). It is remarkable that also in the absence of the salt of transition metal the vinyl chloride polymerization takes place by the action of the system aminoalcohol—carbon tetrachloride though only to a relatively small extent. By substitution of 1-amino-2-propanol with monoethanolamine a trace amount of polymer is formed, whereas diethanolamine and triethanolamine without salt of transition metal do not exert practically any effect in the vinyl chloride polymerization.

The influence of the salts of transition metals as components of the initiation system 1-amino-2-propanol—carbon tetrachloride on vinyl chloride polymerization decreases, as seen from Table 3, in the following sequence:

$$Cu(II) \gg Mn(II), Fe(III), Pb(II), Ni(II), Cr(III), Co(II), Zn(II) > Fe(II) \approx 0.$$
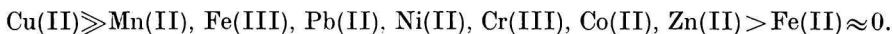
Since in multicomponent initiation systems the rate of vinyl monomer polymerization depends on the concentration of all components of the initiation system [3, 8], we checked the influence of carbon tetrachloride concentration (Table 4), 1-amino-2-propanol (Table 5) and copper(II) acetate (Table 6) respectively, on the rate of vinyl chloride polymerization. With increasing carbon tetrachloride concentration the monomer conversion increases initially in the polymerization system with other additions of carbon tetrachloride bringing about the decrease of polymerization rate. A similar course of the polymerization rate dependence on carbon tetrachloride concentration was observed also in the case of styrene polymerization initiated by the system copper(II) chelate of ephedrine—carbon tetrachloride. Unless the polymerization system comprises halogen-containing compound the polymerization does not occur [6, 8] (Table 4).

On increasing ligand concentration in the polymerization system we observed an increase of vinyl chloride polymerization rate (Table 5). The influence of copper(II) salt concentration over the concentration range 3×10^{-4} to 3×10^{-2} g Cu(II)/ml of vinyl chloride in the system vinyl chloride—1-amino-2-propanol—carbon tetrachloride—copper(II) acetate on vinyl chloride conversion is given in Table 6. When compared with the influence of the change of ligand concentration on vinyl chloride conversion the change of copper(II) salt concentration is not so markedly evident on the values of vinyl chloride conversion. The exponent of the equation expressing dependence of the rate of vinyl chloride polymerization on copper(II) acetate concentration, calculated by means of the data contained in Table 6, has the value of 0.51.

It is remarkable that the rate of vinyl chloride polymerization is not affected by the addition of poly(vinyl chloride) (dead polymer). For the polymerization system, 5 ml of vinyl chloride, 0.3 ml of copper(II) acetate solution, 0.005 g of copper(II) acetate/10 ml of 1-amino-2-propanol and 0.3 ml of carbon tetrachloride, vinyl chloride conversion is 24.5 or 21.0% in case 0.25 or 0.05 g of poly(vinyl chloride) is added to the polymerization system. This is comparable with the vinyl chloride conversion (24.0%) in poly(vinyl chloride)-free system. The data referring to the influence of methanol on vinyl chloride conversion are summarized in Table 7, whereas the conversion decrease is functionally dependent on the decrease of monomer concentration in the system.

The dependence of the rate of vinyl chloride polymerization on the temperature over the range 0—30°C corresponds to the Arrhenius equation (Fig. 1).

From the function dependence shown in Fig. 1 the value of 13.0 kcal mole^{-1} for activation energy was obtained. A typical course of conversion curves of the vinyl chloride polymerization at its initiation by the system 1-amino-2-propanol— —copper(II) acetate—carbon tetrachloride is shown in Fig. 2. By the presence of

Table 3

Influence of transition metal salt on vinyl chloride polymerization initiated by the system 1-amino-2-propanol—salt of transition metal—carbon tetrachloride
Concentration of reaction components: vinyl chloride 5 ml, 0.3 ml of transition metal salt solution in 1-amino-2-propanol, 0.3 ml of carbon tetrachloride
Polymerization temperature 30°C, duration of polymerization 90 minutes

Salt of transition metal*	VC conversion [%]
Cu(II)	24.0
Mn(II)	6.1
Fe(III)	5.6
Pb(II)	2.8
Ni(II)	2.4
Cr(III)	2.3
Zn(II)	2.0
Co(II)	1.3
Fe(II)	**
—	0.9

* The solution of transition metal salt was prepared by dissolving 0.005 g of salt in 10 ml of 1-amino-2-propanol. As salts of transition metals the acetates [Cu(II), Co(II), Fe(III), Pb(II), Zn(II)], chlorides [Ni(II), Cr(III), Mn(II)] and FeSO$_4$ respectively, have been used.
** Does not polymerize.

Table 4

Dependence of vinyl chloride conversion [%] on the concentration of carbon tetrachloride in polymerization system
Vinyl chloride 5 ml, 0.5 ml of copper(II) salt solution (0.005 g Cu(CH$_3$COO)$_2$ · H$_2$O in 10 ml of 1-amino-2-propanol)
Polymerization temperature 30°C, duration of polymerization 1 hour

Carbon tetrachloride [ml]	VC conversion [%]
0	0
0.05	3.3
0.1	13.0
0.3	37.8
0.5	45.3
1.0	44.0
1.5	18.0
3.0	17.5

Table 5

Dependence of vinyl chloride conversion on concentration of 1-amino-2-propanol in the polymerization system: vinyl chloride 5 ml, carbon tetrachloride 0.1 ml, 0.1 ml of copper(II) salt solution (0.005 g $Cu(CH_3COO)_2 \cdot H_2O$ in 10 ml of 1-amino-2-propanol) Polymerization temperature 30°C, duration of polymerization 1 hour

1-Amino-2-propanol [ml]	VC conversion [%]
0.1	0.5
0.4	9.1
0.6	44.7
1.1	51.0
1.5	82.7

Table 6

Dependence of vinyl chloride conversion of copper(II) acetate concentration in the polymerization system: vinyl chloride 5 ml, 1-amino-2-propanol 0.3 ml, carbon tetrachloride 0.3 ml Polymerization temperature 30°C, duration of polymerization 90 minutes

$\dfrac{\text{g Cu(II)} \times 10^4}{100 \text{ ml VC*}}$	Conversion [%]
100	30.9
30	24.0
6	7.0
3	5.1

* Volume of vinyl chloride at temperature −78°C.

Table 7

Dependence of vinyl chloride conversion on methanol concentration in the polymerization system: vinyl chloride 5 ml, copper(II) salt solution (0.005 g $Cu(CH_3COO)_2 \cdot H_2O$ in 10 ml of 1-amino-2-propanol) 0.3 ml, carbon tetrachloride 0.3 ml Polymerization temperature 30°C, duration of polymerization 90 minutes

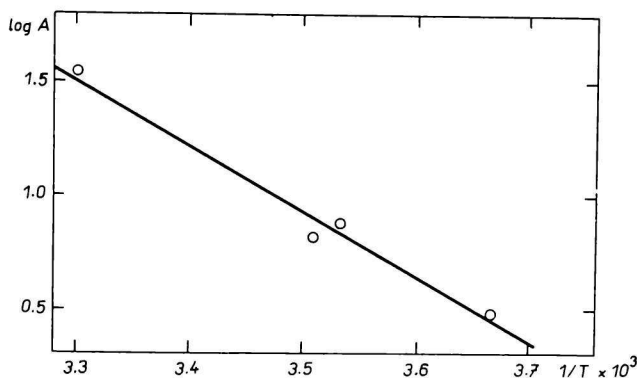| Methanol [ml]	VC conversion [%]
0	24
0.1	23.8
0.3	24.3
0.5	12.8
1.0	11.9
1.15	10.4
1.30	7.9
1.50	6.3

Fig. 1. Arrhenius dependence for vinyl chloride polymerization initiated by the system
1-amino-2-propanol—copper(II) acetate—carbon tetrachloride.
Vinyl chloride 5 ml, copper(II) salt solution (0.005 g of copper(II) acetate/10 ml cf
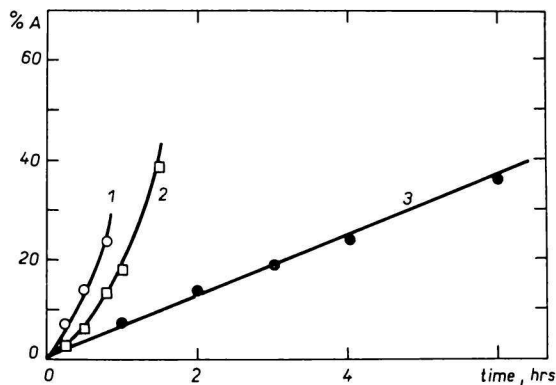1-amino-2-propanol) 0.5 ml, carbon tetrachloride 0.5 ml.

Fig. 2. Dependence of vinyl chloride conversion in polymerization initiated by the
system 1-amino-2-propanol—copper(II) acetate—carbon tetrachloride on the duration
of polymerization.
Curve 1: vinyl chloride 5 ml, carbon tetrachloride 0.5 ml, copper(II) salt solution
(0.005 g of copper(II) acetate/10 ml of 1-amino-2-propanol) 0.5 ml, polymerization
temperature 30°C.
Curve 2: vinyl chloride 5 ml, carbon tetrachloride 0.1 ml, copper(II) salt solution
(0.005 g of copper(II) acetate/10 ml of 1-amino-2-propanol) 0.5 ml, polymerization
temperature 30°C.
Curve 3: vinyl chloride 5 ml, carbon tetrachloride 0.5 ml, copper(II) salt solution
(0.005 g of copper(II) acetate/10 ml of 1-amino-2-propanol) 0.5 ml, polymerization
temperature 10°C.

transfer agent (carbon tetrachloride) in certain concentration ratios, a linear time course of monomer conversion may be obtained (Fig. 2).

To account for the initiation mechanism of vinyl monomer polymerization by the system organic ligand—salt of transition metal—halogen-containing compound, the notion of a reaction mechanism suggested for interaction of copper(II) chelate (—)-ephedrine with carbon tetrachloride [11] may well be used. In the course of oxidation-reduction reaction taking place between chelate and carbon tetrachloride, the transfer of the electron from the ligand brings about the formation of carbon tetrachloride anion which decomposes immediately into trichloromethyl radical and chloride anion. Trichloromethyl radicals formed initiate the polymerization of vinyl monomer present in the reaction system. In the course of the interaction of chelate with carbon tetrachloride both the reduction of the central metal of chelate and the ligand oxidation take place. The reduction of central atom and the oxidation products were proved experimentally [4, 8, 11]. In the polymerization system containing ligand and salt of transition metal the formation of chelate complex takes place as well, whereas, however, the prevailing part of ligand is "free", *i.e.* non-bonded with the compound of the transition metal in the complex. The second alternative is provided by the notion of chain-radical mechanism suggested for the reaction of aliphatic amines with carbon tetrachloride in the presence of copper or iron salts [10]. According to this mechanism, the decrease of oxidation degree of transition metal is primarily brought about by the reaction with amine under the formation of amine radical. The formation of trichloromethyl radicals takes then place by the reaction of carbon tetrachloride with the formed complex compound of the transition metal in lower oxidation degree.

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