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INITIATION OF VINYL POLYMERIZATION BY SYSTEM BIVALENT COPPER–AMINOALCOHOL–CARBON TETRACHLORIDE

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Abstract—In this paper there are preliminary results of investigations of initiation of vinyl polymerization by the system aminoalcohol–carbon tetrachloride–copper salt. As aminoalcohol (−)-ephedrine and 2-diethylaminoethanol were used. The copper salt was represented by copper acetate, stearate and chloride. It can be inferred from the results of polymerization experiments that ephedrine is a more efficient component of the initiator in styrene polymerization than diethylaminoethanol. Between the efficiency of the copper acetate and stearate, no differences were observed. From the evaluation of ESR spectra, it appears that reduction of the bivalent copper is occurring in the initiation system. Electron transfer from the aminoalcohol to carbon tetrachloride and formation of trichloromethyl radicals is supposed.

In our previous paper we showed that *bis*-(−)-ephedrine copper (II) chelate reaction with carbon tetrachloride can be used for initiating radical reactions.(1) The supposed mechanism of this reaction involves the existence of radical intermediates and leads finally to formation of reaction products of the oxidation of the ligand and to the reduction of the bivalent copper of the chelate.(2) To a certain extent, an analogous reaction mechanism is known also with the aliphatic (aromatic) system amine–carbon tetrachloride–transition metal salt.(3) Such three-component systems give best results in investigations of olefin telomerization; for initiation of polymerizations, less attention was paid to them. In this last connection, the paper of Fueno *et al.*(4) on the influence of the system dimethyl aniline–benzyl chloride on the polymerization of methyl methacrylate and the paper of Imoto *et al.*(5) on the effect of the system imidazol-carbon tetrachloride on the polymerization of vinyl monomers, are noteworthy.

In this paper we give an account of preliminary results of investigations of the initiating system aminoalcohol–carbon tetrachloride–copper salt as well as on the effect of the respective components of the system in various combinations on the polymerization rate of the vinyl monomer. Some of these systems were also studied by the ESR method.

EXPERIMENTAL

The polymerization solutions were prepared by mixing the copper salt and aminoalcohol in the monomer with a solution of carbon tetrachloride in the monomer. The inhibitor was removed from the monomers by shaking with aqueous sodium hydroxide and after drying monomers were distilled at reduced pressure of nitrogen. Polymerization was accomplished in glass ampoules sealed under argon. Conversion of the monomer was determined gravimetrically. Electron spin resonance spectra of the solutions containing paramagnetic Cu^{2+} ions were recorded on a RE 1301 radiospectrometer. The copper salt and the (−)-ephedrine were weighed in the measuring ampoules which were sealed under argon. The measuring was carried out at 60°; at this temperature at a particular moment, carbon tetrachloride was dosed into the reaction system by means of a syringe. At the same time care was taken to preserve the inert atmosphere in the measured sample. The concentration determinations were calibrated by DPPH as standard.

RESULTS AND DISCUSSION

From data listed in Table 1, several conclusions can be made. First of all, there is the discovery that the rate of polymerization of styrene, if initiated by the aminoalcohol–copper salt–carbon tetrachloride system, is influenced by the kind of the aminoalcohol used. (—)-ephedrine seems to be more efficient than 2-diethylaminoethanol whether in presence of the copper salt or in its absence. On the other hand, no substantial differences of polymerization rate arose from substituting cupric acetate for copper stearate. Similarly no differences of polymerization rate were observed in initiation of polymerization by the system *bis*-(—)-ephedrine copper (II) chelate–carbon tetrachloride, pointing to the possibility of an analogous initiation mechanism in both cases (see below).

TABLE 1. RESULTS FOR POLYMERIZATION OF A VINYL MONOMER UPON INITIATION BY THE SYSTEM AMINOALCOHOL–COPPER SALT–CARBON TETRACHLORIDE. TEMPERATURE 60°

Run No.	Copper compound	Mole l^{-1} $.10^3$	Aminoalcohol*	Mole l^{-1} $.10^2$	Carbon tetrachloride mole l^{-1}	Monomer*	$R_p .10^5$ mole l^{-1} sec $^{-1}$
1	Acetate	5·0	EPH	2·5	0·1	S	8·82
2	Acetate	5·0	EPH	2·5	—	S	0·0
3	Stearate	5·0	EPH	2·5	0·1	S	10·65
4	Acetate	0·50	DEAE	10·0	0·1	S	5·13
5	Acetate	1·25	DEAE	10·0	0·1	S	6·76
6	Acetate	2·50	DEAE	10·0	0·1	S	8·41
7	Acetate	5·0	DEAE	2·9	0·1	S	2·8
8	Acetate	5·0	DEAE	4·2	0·1	S	3·5
9	Acetate	5·0	DEAE	5·5	0·1	S	4·1
10	Acetate	5·0	DEAE	6·8	0·1	S	4·8
11	Acetate	5·0	DEAE	8·1	0·1	S	5·3
12	Acetate	5·0	DEAE	2·5	—	S	0·0
13	Acetate	2·5	DEAE	2·5	0·1	M	9·96
14	Acetate	1·0	DEAE	2·5	0·1	M	7·96
15	Chloride†	—	EPH	—	0·1	S	2·66
16	Chloride†	—	DEAE	—	0·1	S	0·0
17	—	—	DEAE	2·5	0·1	S	0·4‖
18	—	—	DEAE	2·5	—	S	0·0
19	—	—	EPH	2·5	0·1	S	2·5‖
20	—	—	EPH	2·5	—	S	1·0‖
21	KEZ‡	5·0	—	—	0·1	S	0·0
22	KEZ‡	5·0	EPH	2·5	—	S	8·78
23	Chelate§	5·0	—	—	0·1	S	8·41

* EPH : (—)-ephedrine DEAE : 2-diethylaminoethanol
S : styrene M : methyl methacrylate.

† Cupric chloride reacted immediately with aminoalcohol after mixing. For the polymerization the transparent solution over the resulting precipitate was used.

‡ KEZ is a green solution of the *bis*-(—)-ephedrine copper (II) chelate in carbon tetrachloride used 1 hr after dissolving the chelate in carbon tetrachloride.

‖ Per cent of monomer conversion after 1 hr of polymerization.

§ *bis*-(—)-ephedrine copper (II) chelate.

The effect of the concentration of the copper salt in the system cupric acetate–ephedrine–carbon tetrachloride on the rate of polymerization of styrene is characterized by the value of the exponent $n = 0{\cdot}30$ in the equation $R_p = k$ [copper acetate]^n

for styrene and $n = 0 \cdot 25$ for methyl methacrylate. Both values are close to the value $n = 0 \cdot 26$ found in polymerization of styrene initiated by the system *bis*-(—)-ephedrine copper (II) chelate–carbon tetrachloride.(1) For the dependence of polymerization rate of styrene on concentration of 2-diethylaminoethanol for the system cupric acetate-2-diethylaminoethanol–carbon tetrachloride, the value of $n = 0 \cdot 61$ was found.

Initiation of polymerization of the vinyl monomer occurs even in absence of the copper salt. Under these conditions, more pronounced initiation effects were found with the combination (—)-ephedrine–carbon tetrachloride than with the system 2-diethylaminoethanol–carbon tetrachloride. The causes of the different behaviour for the aminoalcohols are supposed to lie in the different oxidizing capability i.e. the facility of electron release upon interaction with carbon tetrachloride. The data on polymerizations initiated by the systems aminoalcohol–carbon tetrachloride–cupric chloride, because of formation of a heterogeneous system (see remark to Table 1), can be considered as indicative only, although differences between ephedrine and 2-diethylaminoethanol can be observed. When initiating polymerization of styrene by a solution of *bis*-(—)-ephedrine copper (II) chelate in carbon tetrachloride provided the latter is used approximately 1 hr after its preparation i.e. in presence of reaction products of the decomposition of the chelate, the resulting green solution displays a low initiating efficiency in comparison with a freshly prepared violet solution of the *bis*-(—)-ephedrine copper (II) chelate in carbon tetrachloride. As we have shown in another paper,(6) the green solution of *bis*-(—)-ephedrine copper (II) chelate even after a long period from its preparation (2–3 hr) still contains a measurable quantity of paramagnetic Cu^{2+} ions. We estimate therefore that the reduction of polymerization rate of styrene is caused by the low concentration of components capable of initiating the polymerization rather than by a retarding effect of decomposition products of the chelate. The addition of ephedrine to this initiating system increases substantially the polymerization rate of styrene which is in accordance with the observed initiating effect of the system ephedrine–carbon tetrachloride.

It follows from concentration measurements of paramagnetic Cu^{2+} ions that in the mixture cupric chloride-(—)-ephedrine a change of concentration of Cu^{2+} ions occurs before addition of carbon tetrachloride while in the copper acetate system this change occurs only after addition of carbon tetrachloride to the system. For calculation of rate constants characterizing the reaction $Cu^{2+} + CCl_4 \xrightarrow{k} Cu^{1+}$ the equation for pseudomonomolecular reaction was used. The calculated values of the rate constants are listed in Table 2.

TABLE 2. CALCULATED VALUES OF RATE CONSTANTS OF THE REACTION $Cu^{2+} + CCl_4 \xrightarrow{k} Cu^{1+}$ FOR THE SYSTEMS COPPER COMPOUND–AMINOALCOHOL–CARBON TETRACHLORIDE. TEMPERATURE 60°

Copper compound	$k.10^4$ mole^{-1} l.sec^{-1}
Cupric acetate*	6·7
Cupric chloride†	5·6
Bis-(—)-ephedrine copper (II) chelate	2·8

* Components in reaction system were dosed as follows: Cupric acetate : ephedrine : carbon tetrachloride 1 : 20 : 200 (molar).

† Components in reaction systems were dosed as follows: Cupric chloride : ephedrine : carbon tetrachloride 1 : 10 : 100 (molar).

In this case a precipitate was observed in the reaction system.

Comparing the results of polymerization experiments with those obtained by means of ESR, we suppose that, as with the system *bis*-(—)-ephedrine copper (II) chelate–carbon tetrachloride, an electron transfer to carbon tetrachloride occurs for the system aminoalcohol–carbon tetrachloride; this leads to formation of a trichloromethyl radical and, in presence of a copper compound in the reaction system, also to a reduction of the valency of copper. In the presence of a vinyl monomer, trichloromethyl radicals start the polymerization reaction. However it cannot be ruled out that, in the initiation of polymerization reactions, there is participation also from other intermediates forming during interaction of the aminoalcohol with carbon tetrachloride, or in subsequent reactions.

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