Radical reactions initiated by chelate complexes of transition metals. VIII.

System poly(vinyl chloride)—bis(—)ephedrine copper(II) chelate as initiator of vinyl polymerization

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The system poly(vinyl chloride)—bis(—)ephedrine copper(II) chelate as initiator of n-butyl methacrylate polymerization in cyclohexanone has been investigated. It has been found that with increasing monomer concentration the exponent value for [chelate] in the expression for polymerization rate decreases. Thus for [BuMc] = 0.78 and 3.14 mol l^{-1}, the exponents are 0.23 and 0.17, respectively. The dependence of polymerization rate on monomer concentration suggests that the monomer does not participate in the initiation reaction, *i.e.* that the exponent for monomer concentration in the expression for polymerization rate equals one.

From the data on polymerization rate of n-butyl methacrylate at various temperatures over the range 50—90°C the activation energy of 23.4 kcal mol^{-1} has been calculated. It was found that under the conditions of $[\text{Cl}]_{\text{PVC}}/[\text{chelate}] \geqq 1$, the polymerization rate of n-butyl methacrylate was practically independent of poly(vinyl chloride) concentration. By a convenient choice of poly(vinyl chloride) and monomer concentration the initiation system investigated enables the preparation of reaction products of quite a high abundance of poly(vinyl chloride) component, *i.e.* either a grafted copolymer or practically pure homopolymer of poly(n-butyl methacrylate), in which the concentration of the poly(vinyl chloride) component is negligible.

The study of the reaction of bis(—)ephedrine copper(II) chelate with halogen-containing low-molecular [1, 2] or high-molecular [3] compounds was dealt with in our previous papers. We found the halogen-containing compounds polysubstituted on the same carbon to be most effective in the reaction with Cueph, whereas the di- or monosubstituted halogen-containing compounds were less reactive. In the course of chelate interaction with halogen-containing compounds the formation of radical intermediates capable of initiating polymerization reactions [2] is presumed to take place. In the case of high-molecular halogen-containing polymer the reaction mechanism considered leads to the formation of the grafted copolymer from the halogen-containing polymer and monomer added to the reaction system [3, 4].

Abbreviations:

BuMc n-butyl methacrylate.

Cueph bis(—)ephedrine copper(II) chelate.

In the present paper intended to find the influence of monomer and chelate concentration on the kinetics of polymerization at constant concentration of the poly(vinyl chloride) component in the reaction mixture, results of the study of *n*-butyl methacrylate polymerization initiated by the system poly(vinyl chloride)—bis(—)ephedrine copper(II) in cyclohexanone are dealt with.

Experimental

Chemicals used and their purification

Poly(vinyl chloride) suspension of Montecatini Edison S.p.A. Sicron 548 FM was used. Cueph was prepared according to [1]. The monomer *n*-butyl methacrylate, commercial product of laboratory grade was purified by shaking with 10% solutions of sodium hydroxide, sulfuric acid, and sodium carbonate in the indicated sequence and washed with distilled water. After drying with calcium chloride the monomer was stored in a refrigerator. Before being used for polymerization the monomer was distilled at a reduced nitrogen pressure. Cyclohexanone (purum) was heated with 1 weight % of iron(II) sulfate (anal. grade) and bubbled with nitrogen at 90°C for 90 minutes. The insoluble portion was filtered off and, after drying with calcium chloride, cyclohexanone was distilled in nitrogen atmosphere (n_D^{25} 1.4481). Methanol, a technical product, was distilled before use.

Polymerization technique

Into glass test tubes, length 18 cm, inner diameter 10 mm, wall thickness 1.5 mm, contracted at the distance of about 8 cm apart from the bottom and blown by bulb nitrogen purified by letting them pass through the column with active copper at 200°C and dried in a drier with silica gel, solution of poly(vinyl chloride) in cyclohexanone (0.1 g/2 ml cyclohexanone) and that of Cueph in *n*-butyl methacrylate so that the resulting polymerization solution be 4 ml, are pipetted separately. After blowing with pure nitrogen the ampoules were sealed at the place contracted and inserted into a tempered bath. At fixed time intervals the ampoules were taken out, the polymer being precipitated with methanol. The polymer thus precipitated was dried to constant weight in a vacuum drier at reduced pressure (5 torr, 60°C).

Determination of specific viscosity

For the determination of specific viscosity ($\eta_{sp} = \eta_{rel} - 1$) of poly(vinyl chloride) in the mixtures of cyclohexanone and *n*-butyl methacrylate Ubbelohde's viscosimeter was used, poly(vinyl chloride) concentration being invariably 2.5 g/100 ml. From the data on the flow times of the solutions of poly(vinyl chloride) and the mixtures of solvent with monomer, relative viscosity η_{rel} as the ratio of the flow times t/t_0 after application of the correction for kinetic energy was determined. All of the measurements were made at 25 ± 0.02°C.

Results and discussion

Influence of bis(—)ephedrine copper(II) chelate on the polymerization rate of n-butyl methacrylate

The influence of Cueph concentration was investigated at the *n*-butyl methacrylate concentrations 0.78 and 3.14 mol l^{-1}, respectively. The conversion curves are linear at

Table 1

Dependence of polymerization rate of *n*-butyl methacrylate in cyclohexanone in the presence of poly(vinyl chloride) (25 g l^{-1}) on bis(—)ephedrine copper(II) chelate concentration

[*n*-Butyl methacrylate] [mol l^{-1}]	[Cueph] · 10^4 [mol l^{-1}]	$R_p \cdot 10^4$ [mol l^{-1} s^{-1}]
0.78	1	0.19
	5	0.32
	50	0.46
	500	0.70
3.14	1	1.48
	5	2.00
	10	2.26
	50	2.88
	500	2.53

least up to 10% conversions. At high concentrations of Cueph in the polymerization system the decrease of polymerization rate takes place as expression of the increased chelate participation in termination reactions with radicals. The polymerization rates calculated are shown in Table 1. In Fig. 1 dependence of polymerization rate on Cueph concentration (values taken from Table 1), linear in logarithmic coordinates is shown. By analyzing the plots shown in Fig. 1 for the reaction order with respect to [Cueph] for monomer concentrations 0.78 and 3.14 mol l^{-1} the exponents 0.23 and 0.17 were obtained, respectively. The low values of exponents for [Cueph] suggest the participation of primary radicals in termination reactions with chelate. The mechanism of this reaction is similar to that of radical termination in the presence of iron(III) chloride [5]. In our opinion, the decrease of exponent value for [Cueph] in the medium containing higher *n*-butyl methacrylate concentration (3.14 mol l^{-1} *vs.* 0.78 mol l^{-1}) is due to conformation changes of poly(vinyl chloride) molecule in increasing precipitant — monomer concentration,

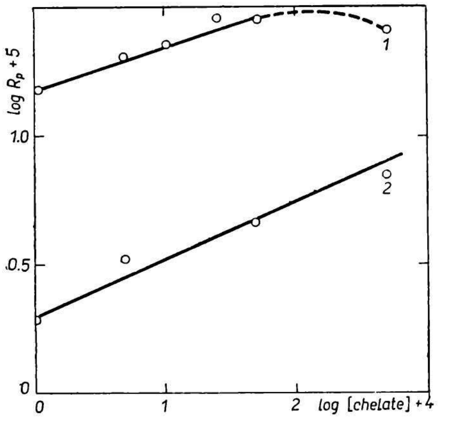

Fig. 1. Dependence of log of *n*-butyl methacrylate polymerization rates in cyclohexanone in the presence of poly(vinyl chloride) on log of bis(—)ephedrine copper(II) chelate concentration.
Temperature 60°C, data taken from Table 1.
1. [BuMc] = 3.14 mol l^{-1}; *2.* [BuMc] = = 0.78 mol l^{-1}.

as well as to preference sorption. The forming fluctuations of monomer concentration in the neighbourhood of poly(vinyl chloride) macromolecule affect the addition reaction of the monomer on radical centres situated on poly(vinyl chloride) macromolecule. On the other hand, these phenomena do not affect Cueph interaction with these radical centres so that the resulting effect of these factors is the increase of the share of termination reactions of radicals with Cueph. The change of the size of poly(vinyl chloride) macromolecule coil may well be suggested from viscosimetric measurements, though, as a matter of fact, these measurements cannot reflect local concentration fluctuations. By adding *n*-butyl methacrylate to cyclohexanone decrease of specific viscosity (Table 2), when compared with its value for pure cyclohexanone poly(vinyl chloride) solution, is brought about.

Table 2

Dependence of specific viscosity η_{sp} of poly(vinyl chloride) in the mixture of cyclohexanone—*n*-butyl methacrylate on *n*-butyl methacrylate concentration
Poly(vinyl chloride) concentration 2.5 g/100 ml; temperature 25°C

[BuMc] [mol l^{-1}]	η_{sp}
—	5.25
1.57	4.55
2.35	4.35
3.14	4.35
3.92	4.70

Influence of n-butyl methacrylate concentration on polymerization rate

The influence of *n*-butyl methacrylate concentration in the system *n*-butyl methacrylate—cyclohexanone—poly(vinyl chloride)—Cueph was investigated under conditions preventing the precipitation of poly(vinyl chloride) from the reaction mixture. There was an exception in the case of polymerization in the absence of cyclohexanone, *i.e.* under

Table 3

Dependence of polymerization rate of *n*-butyl methacrylate in cyclohexanone in the presence of poly(vinyl chloride) (25 g l^{-1}) and bis(—)ephedrine copper(II) chelate (5×10^{-3} mol l^{-1}) on *n*-butyl methacrylate concentration
Temperature 60°C

[BuMc] [mol l^{-1}]	$R_p \cdot 10^4$ [mol l^{-1} s^{-1}]	[BuMc] [mol l^{-1}]	$R_p \cdot 10^4$ [mol l^{-1} s^{-1}]
4.70	3.79	2.35	1.70
3.92	3.48	1.57	1.05
3.14	2.88	0.78	0.46

the conditions of poly(vinyl chloride) suspended in the reaction medium. Using data from Table 3 Fig. 2 was plotted showing the dependence of log of polymerization rates on log of n-butyl methyl methacrylate concentrations. The order with respect to n-butyl methacrylate concentration in expression for polymerization rate is one (1.2). This result suggests no participation of monomer in the initiation reaction. Similarly, in the case of styrene polymerization initiated by the system Cueph—carbon tetrachloride [2] a unit exponent for monomer concentration in the expression for polymerization rate was found. In the absence of cyclohexanone, n-butyl methacrylate conversion in the polymerization at 60°C after 3 hours and poly(vinyl chloride) concentration of 25 g l^{-1} and Cueph 5×10^{-3} mol l^{-1} was 3.8%, *i.e.* considerably lower than in the case of the polymerization in the presence of cyclohexanone.

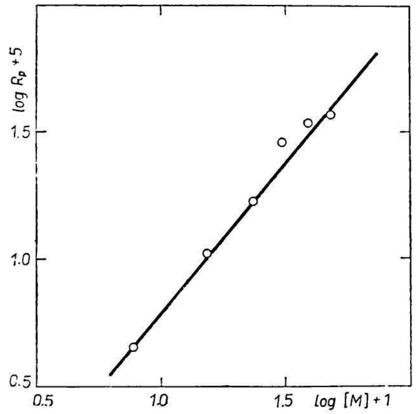

Fig. 2. Dependence of log of n-butyl methacrylate polymerization rates in cyclohexanone in the presence of poly(vinyl chloride) and bis(—)ephedrine copper(II) chelate on log of n-butyl methacrylate concentration.
Temperature 60°C, data taken from Table 3.

Using Arrhenius equation the activation energy of 23.4 kcal mol^{-1} was determined from the temperature-dependent polymerization rate of n-butyl methacrylate (Table 4). The drop of polymerization rate at 90°C suggests that there should be an increase in the share of termination reactions of radicals with Cueph. Since the activation energy of this interaction lies within the range 5—10 kcal mol^{-1} [6], and the activation energy of the

Table 4

Dependence of polymerization rate of n-butyl methacrylate in cyclohexanone in the presence of poly(vinyl chloride) (25 g l^{-1}) and bis(—)ephedrine copper(II) chelate (5×10^{-3} mol l^{-1}) on the temperature
Concentration of n-butyl methacrylate 3.14 mol l^{-1}

Temperature [K]	$R_p \cdot 10^4$ [mol l^{-1} s^{-1}]
323	0.87
333	2.88
343	8.75
353	11.6
363	3.62

propagation reaction is about 5 kcal mol^{-1} [7], the termination reactions of radicals with chelate are more preferable at higher temperatures. Neither the effect of the chelate deactivation at this temperature, as a result of chemical changes on its ligands, may be excluded.

Evaluation of the extent of chlorine atoms utilization in poly(vinyl chloride) in the reaction with bis(—)ephedrine copper(II) chelate

The problem of the extent of chlorine atoms utilization in the reaction with Cueph has been dealt with in our previous paper [3]. Using the technique of subsequent polymerizations which substantially meant the repetition of polymerization with the reaction product obtained from the preceding polymerization we have found the polymerization rates in three subsequent polymerizations 2.82, 2.51, and 2.04×10^{-4} mol l^{-1} s^{-1}, respectively. This was carried out under the following reaction conditions. Concentration of PVC or of the product of its grafting for the second and third polymerization was 25 g l^{-1}, [BuMc] = 3.14 mol l^{-1}, [Cueph] = 5×10^{-3} mol l^{-1}, temperature 60°C, using cyclohexanone as solvent. In this case, the decrease of polymerization rate is considerably lower than in that of methyl methacrylate telomer [3] which is given, as a matter of fact, by a substantially higher starting concentration of chlorine atoms in PVC, when compared with the telomer used. This result is in agreement with previous findings [2] that the polymerization rate is slightly dependent on the concentration of the donor of chlorine atoms provided that $[Cl]/[Cueph] \geqq 1$, and the monomer concentration is constant.

By repetition of the subsequent polymerizations, the poly(vinyl chloride) concentration in reaction products decreases gradually. After the first, second, and third polymerization, 59, 95, and 99 weight %, respectively of poly(n-butyl methacrylate) were present in the reaction product for the three cases referred to. The calculation was carried out according to the n-butyl methacrylate conversion found.

These results lead to the two conclusions: first, that the polymerization rate of n-butyl methacrylate initiated by the system poly(vinyl chloride)—Cueph is sufficiently high even at relatively low halogen donor concentration and second, that by convenient choice of starting concentrations of reactants, reaction products with high or low content of poly(vinyl chloride) may be prepared, *i.e.* the synthesis aimed at the preparation of grafted poly(vinyl chloride) or practically pure n-butyl methacrylate homopolymer. In the last example indicated, poly(vinyl chloride) serves only as a component of the initiation system, the influence of the latter on the physical properties of the polymerization product being practically negligible.

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