Radical Reactions Initiated by Chelate Complexes of Transition Metals. 16. Modification of Vinyl Chloride Oligomer

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ABSTRACT

The reaction kinetics and characterization of the reaction
products of the modification of the vinyl chloride oligomer
containing -CCl_3 end groups by n-butyl methacrylate in the
presence of copper (II) ephedrinate was studied. The reaction
product contains three high molecular weight components: modi-
fied poly(vinyl chloride) (copolymer), unchanged vinyl chloride
oligomer, and poly(n-butyl methacrylate) homopolymer. The
extent of the modification process depends on the molar ratio
between the concentration of the halogen-containing groups
utilizable for the reaction with metal chelate and on the
concentration of metal chelate. If there is a molar excess of
chelate compared with the molar concentration of -CCl_3 end
groups in vinyl chloride oligomer, then other halogen-containing
groups besides -CCl_3 end groups of vinyl chloride oligomer are
used in the formation of modified poly(vinyl chloride). This
enables incorporation of more than two poly(n-butyl methacrylate)
sequences into the poly(vinyl chloride) chain.

Several years ago, Kastning [1] published a paper on the ability
of certain metal chelates to initiate free-radical polymerization of
unsaturated monomers. It was shown [1] that in the presence of
halogen-containing compounds the polymerization rate increased
markedly. The interaction between copper (II) ephedrinate (Cueph)
and carbon tetrachloride leads to the dissociation of one of the C–Cl
bonds in carbon tetrachloride, with formation of a trichloromethyl
radical [2]. This reaction mechanism of free-radical formation is
valid also for a high-molecular weight halogen-containing compound,
such as a halopolymer, instead of carbon tetrachloride. In this case
the halopolymer molecule, analogously to the trichloromethyl radical,
forms a part of a new polymer, e. g., block and/or graft copolymers
of halopolymer are formed [3]. The structure of the copolymer can
be "tailored" by introducing reactive groups, such as trichloromethyl,
dichloromethyl, or dibromomethyl groups into the macromolecule.
If there are halogen-containing groups at the end of the macromole-
cule, the formation of block copolymers should occur. Graft copoly-
mers are formed from polymers containing reactive groups in the
middle of the macromolecular chain. When the system halopolymer-
metal chelate was used, block and graft copolymers from chlorinated
polyolefins, chlorinated natural rubber, poly(vinyl chloride), various
vinyl polymers (containing trichloromethyl groups at the end of
macromolecule) and styrene, methyl methacrylate, butyl methacry-
late, acrylonitrile, diallyl phthalate, divinylbenzene, and triallyl
cyanurate were prepared [3-6].

In this paper we report on further results of the study of the
metal chelate-halopolymer interaction in the presence of n-butyl
methacrylate and on the characterization of reaction products thus
obtained. A vinyl chloride oligomer containing -CCl$_3$ end groups [7]
was used as the halopolymer, and copper (II) ephedrinate was the metal
chelate.

EXPERIMENTAL

Chemicals

Commercial n-butyl methacrylate (Lachema, Czechoslovakia) was
freed of inhibitor by shaking successively with 10% aqueous sodium
hydroxide, sulfuric acid, and sodium carbonate and then washing with
distilled water to neutral reaction. It was dried with anhydrous
calcium chloride and distilled twice in a nitrogen atmosphere under
reduced pressure before use.

Rectified vinyl chloride (Chemical Works, Nováky) was dried by
passing it through the column packed with silica gel.

Tetrahydrofuran, carbon tetrachloride, benzene, cyclohexanone

(all analytical grade, Lachema, Czechoslovakia) and 1-amino-2-propanol (Fluka AG, Buchs) were distilled under nitrogen before use.

Methanol, 2-propanol and copper (II) acetate, Cu $(OCOCH_3)_2 \cdot H_2O$, (Lachema, Czechoslovakia) were used without further purification.

Copper (II) ephedrinate, $(C_{10}H_{14}ON)_2 Cu \cdot 2/3\ C_6H_6$ was prepared as described previously [8].

Preparation of Vinyl Chloride Oligomer

Polymerization of vinylchloride was initiated by trichloromethyl radicals arising from the reaction between copper (II) 1-amino-2-propanolate and carbon tetrachloride [7].

The polymerization solution consisted of vinyl chloride (10 ml), tetrahydrofuran (15 ml), carbon tetrachloride (7 ml), and 1-amino-2-propanol (2 ml), containing 1 mg of copper (II) acetate monohydrate. The temperature was 20°C and the reaction time was 3 hr.

After polymerization, tetrahydrofuran (10 ml) was added to the reaction mixture, the polymer was precipitated with methanol and purified by repeated precipitation from hydrofuran solution with methanol. The monomer conversion was 7%. The vinyl chloride oligomer (VCO) prepared had a number-average molecular weight $\overline{M}_n$ of 5000 (by vapor pressure osmometry) and a limiting viscosity number in tetrahydrofuran $[\eta] = 0.145$ dl/g at 25°C.

Synthesis of Modified Poly(vinyl Chloride)

VCO was dissolved in cyclohexanone, and n-butyl methacrylate and a solution of copper (II) ephedrinate in benzene were added. Polymerization was carried out in glass ampoules under argon. Details are given in Tables 1 and 2.

The reaction product P was divided by extraction with benzene into a benzene-soluble (S_1) and a benzene-insoluble (G_1) part. The benzene-soluble material S_1 was further extracted with 2-propanol and the benzene-insoluble material G_1 with a benzene-tetrahydrofuran mixture (10:1 by volume), thus yielding 2-propanol-soluble (S_2) benzene-tetrahydrofuran-soluble (S_3) portions as well as G_2, insoluble in 2-propanol, and G_3, insoluble in benzene/tetrahydrofuran.

Turbidimetry

Turbidimetric titrations of the reaction product and of the products of extraction were performed on an automatic turbidimeter, which has been described elsewhere [9]. Cyclohexanone or tetrahydrofuran were used as solvents, and methanol was the precipitant.

TABLE 1. Initial Polymerization Rates and Limiting Conversion in the System VCO - n-Butyl Methacrylate (BMA) as a Function of the Concentration of Copper (II) ephedrinate (Cueph) and/or VCO[a]

Series	$[VCO]$ (g/dm^3)[b]	$[Cueph] \times 10^3$ (M)	$[VCO]/[Cueph]$ $(mole/mole)$[c]	R_p $(\%/min)$[d]	C_{lim} $(\%)$[e]
A	33.2	0.1	66.4	0.20	20
	33.2	1.0	6.64	0.63	40
	33.2	5.0	1.33	2.06	50
	33.2	10.0	0.66	2.86	75
B	10.0	5.0	0.40	2.36	60
	5.0	5.0	0.20	2.18	60
	2.5	5.0	0.10	1.78	60
	1.0	5.0	0.04	1.45	60

[a]Reaction conditions: $[BMA] = 2.52$ M, $[cyclohexanone] = 4.82$ M, $[benzene] = 1.1$ M; temperature, 70°C.
[b]$\overline{M}_n = 5000$.
[c]VCO per mole of copper (II) ephedrinate in feed.
[d]Initial polymerization rate.
[e]Limiting conversion of n-butyl methacrylate.

Determination of Chlorine

Chlorine in polymers was determined by the Schöniger method [10].

RESULTS AND DISCUSSION

In order to elucidate the character of the course of polymerization of n-butyl methacrylate initiated by the system vinyl chloride oligomer-copper (II) ephedrinate and to evaluate the effect of the composition of the reaction mixture upon the composition of the reaction products, two series of experiments were performed. In series A, the concentration of copper (II) ephedrinate at constant VCO concentration was varied. In series B, the VCO concentration was varied at constant copper (II) ephedrinate concentration.

TABLE 2. Characterization of the Reaction Product of the Modification of VCO by n-Butyl Methacrylate[a]

	Weight %[b]	VC (mole %)	Cloud point V_p/V_s[c]
VC oligomer	-	100.0	1.11
Product P	100.0	34.8	1.15
Benzene-soluble (S_1)	82.1	20.9	2.26
Benzene-insoluble (G_1)	17.9	74.3	1.12
Benzene-soluble (S_1)			
2-propanol-soluble (S_2)	28.9	0.9	2.65
2-Propanol-insoluble (G_2)	53.2	31.6	2.21
Benzene-insoluble (G_1)			
B/THF-soluble (S_3)[d]	4.7	75.3	1.12
B/THF-insoluble part (G_3)[d]	13.2	71.3	1.12

[a]Conditions for preparation: VCO = 41.9 g/dm^3, [Cueph] = 5 × 10^{-4} M, [BMA] = 2.52 M, [cyclohexanone] = 4.82 M, [benzene] = 1.1 M. Temperature, 70°C; reaction time, 3 hr; monomer conversion, 47.9%.
[b]Weight % with respect to reaction product P.
[c]The cloud point during turbidimetric titration; V_p and V_s are the volumes of precipitant (methanol) and of a solution of tetrahydrofuran (0.15 g of polymer component/100 ml of tetrahydrofuran).
[d]Benzene-tetrahydrofuran mixture, 10:1 by volume.

Figures 1 and 2 show the dependence of the monomer conversion on the reaction time for both series. Table 1 lists initial polymerization rates and limiting conversions. The course of conversion curves in both series is nonlinear, the polymerization rate decreasing with time and finally approaching zero, i.e., polymerization does not practically take place anymore. The substantial difference between the two series lies in the fact that the limiting monomer conversion in series A depends on the copper (II) ephedrinate concentration, whereas in series B at constant concentration of copper (II) ephedrinate it is almost the same for all VCO concentrations employed.

Formation of the radical products in reaction systems A and B is conditioned by interaction of the halogen-containing component with copper (II) ephedrinate [3]. As long as the reaction system includes
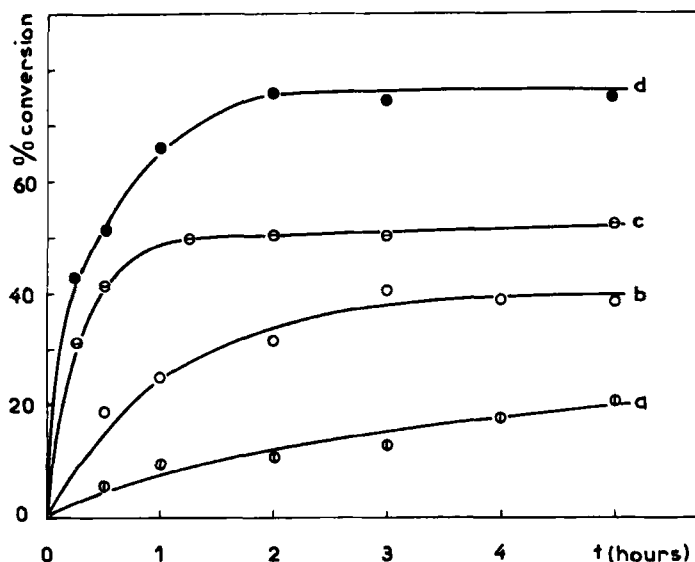
FIG. 1. Dependence of the monomer conversion in the n-butyl methacrylate polymerization initiated by the system VCO-copper (II) ephedrinate on the copper (II) ephedrinate (Cueph) concentration: (a) $[\text{Cueph}]$ = 10^{-4} $\underline{M}$; (b) $[\text{Cueph}]$ = 10^{-3} $\underline{M}$; (c) $[\text{Cueph}]$ = 5×10^{-3} $\underline{M}$; (d) $[\text{Cueph}]$ = 10^{-2} $\overline{\underline{M}}$. Reaction conditions: $[\text{VCO}]$ = 33.2 g/dm^3; $[\text{BMA}]$ = 2.52 $\underline{M}$; $[\text{cyclohexanone}]$ = 4.82 $\underline{M}$; $[\text{benzene}]$ = 1.1 $\underline{M}$; temperature 70°C.

halogen-containing groups, an increase in the copper (II) ephedrinate concentration leads to an increase in both the limiting conversion and the polymerization rate. Of course, if one of the components of the initiating system in consumed, no further initiation of polymerization takes place, and the polymerization rate falls to zero.

As shown previously [8], the reactivity of halogen-containing groups in reaction with copper (II) ephedrinate decreases in the series of halogen-containing alkanes CCl_4 > $CHCl_3$ > CH_2Cl_2. Initiation of polymerization in series A is given predominantly by the interaction of the terminal -CCl_3 groups of VCO with copper (II) ephedrinate. On the other hand, in series B, since $[\text{VCO}] \equiv [-CCl_3]$ < $[\text{Cueph}]$, also the interaction of copper (II) ephedrinate with halogen-containing groups of VCO within a macromolecule [6], most probably with those activated by structural defects of the PVC chain, takes place. It has been shown that the reactivity of PVC during reaction with copper (II) ephedrinate depends on the type of initiating
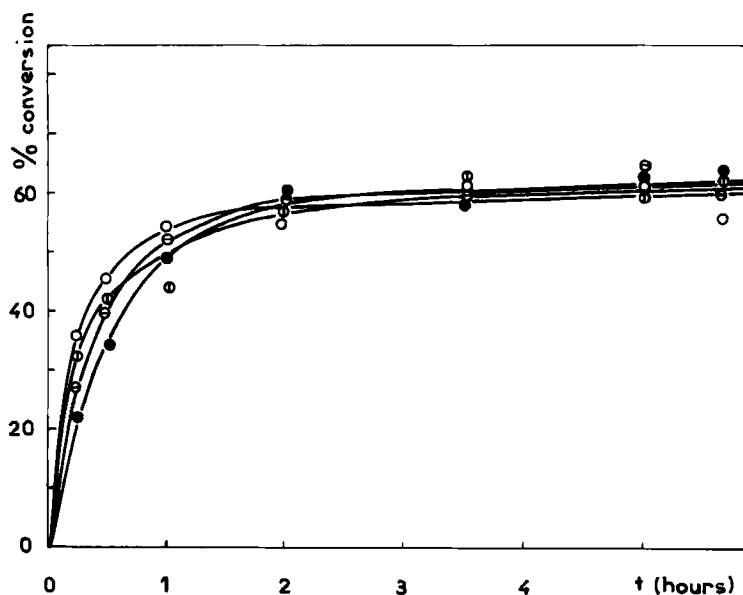
FIG. 2. Dependence of the monomer conversion in the n-butyl methacrylate polymerization initiated by the system VCO - copper (II) ephedrinate on the VCO concentrations: (○) [VCO] = 10 g/dm^3; (⊙) [VCO] = 5 g/dm^3; (⊖) [VCO] = 2.5 g/dm^3; (●) [VCO] = 1 g/dm^3. Reaction conditions: [Cueph] = 5 × 10^{-3}; [BMA] = 2.52 M; [cyclo-hexanone] = 4.82 $\underline{M}$; [benzene] = 1.1 $\underline{M}$; temperature 70°C.

system of VC polymerization employed [4, 6]. The limiting conversion of monomer (series B) achieved regardless of the concentration of the terminal -CCl$_3$ groups leads to the conclusion that other halogen-containing groups also participate in the interaction with copper (II) ephedrinate. The reactivity of these groups is lower than that of the -CCl$_3$ groups, which is manifested by the lower initial polymerization rate.

Results of the division of the reaction products of VCO modification by selective extractions and turbidimetric titration are compiled in Table 2 and Fig. 3. Consecutive extractions with benzene and 2-propanol yielded pure homopolymer of poly(n-butyl methacrylate) (S$_2$) and VCO-BMA (G$_2$). Taking into account the results obtained by extraction with benzene and 2-propanol as well as the material balance, one can conclude that the benzene-insoluble product G$_1$ contains both unchanged VCO and a VCO-BMA copolymer with a higher content of VC units (> 32 mole %). With a mixed solvent
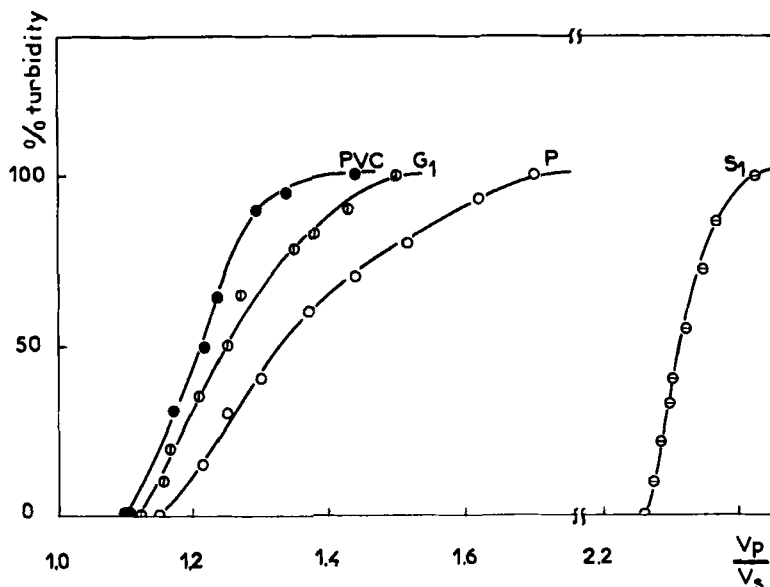
FIG. 3. Turbidimetric titration of VCO and products of its modifi-
cation by n-butyl methacrylate: (PVC) vinyl chloride oligomer; (P)
reaction product P of VCO modified by n-butyl methacrylate (before
extractions); (G_1) benzene-insoluble part of P; (S_1) benzene-soluble
part of P; V_p = volume of the precipitant; V_s = volume of the solvent.

(benzene-tetrahydrofuran, volume ratio 10:1) we succeeded in dividing
the G_1 product into a soluble (S_3) and an insoluble (G_3) component.
Both these components are a mixture of the VCO - BMA copolymer
with higher content of VC units. ($>$ 32 mole %) and of the unreacted
VCO.

The presence of unchanged VCO in the reaction product is given
by the fact that the ratio [VCO] $\gg$ [Cueph] has been chosen for pre-
paring the modified oligomer. With regard to the considered mech-
anism of the initiation of polymerization in the system halogen-
containing polymer-copper (II) ephedrinate [3], poly(n-butyl methac-
rylate) is formed by transfer reactions of polymer radicals with
monomer, since the initiation of the polymerization of monomer does
not occur on interaction with copper (II) ephedrinate.

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