Initiation of the emulsion polymerization of vinyl chloride by the system of carbon tetrachloride and O- or N-containing organic compound

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The initiation system formed by polyhalogenalkanes, mainly by carbon tetrachloride and O- or N-containing organic compound, was investigated in the case of the emulsion polymerization of vinyl chloride. CCl_4 was found to be the most effective, the effectiveness of $CHCl_3$ is one fifth of CCl_4; $Cl_2CHCHCl_2$ and $Cl_2C=CCl_2$ have virtually no influence on polymerization. From among oxygenous compounds especially alkali cellulose, lignin with sodium hydroxide, alkaline hemicelluloses, paraldehyde, dioxan, ethylene oxide, acetals, and ascorbic acid; from among N-containing compounds morpholine, piperidine, and allylamine are effective.

Aqueous solution of an emulsifier is most suitable, methanol to a lesser degree, and water is the least effective.

The mechanism of the formation of initiation system as well as of the initiation of polymerization itself have been discussed.

На примере эмульсионной полимеризации винилхлорида исследована инициационная система, образованная полугалогеналканами, особенно тетрахлорметаном и кислородсодержащим, или же азотсодержащим органическим веществом. Из полигалогеналканов самым действенным является CCl_4, приблизительно 1/5 действенность имеет $CHCl_3$, $Cl_2CHCHCl_2$ и $Cl_2C=CCl_2$ являются почти бездейственными. Из кислородсодержащих веществ действенной является особенно алкалицеллюлоза, лигнин с гидроокисью натрия, алкалические гемицеллюлозы, паральдегид, диоксан, окись этилена, ацетали и аскорбиновая кислота. Из азотсодержащих веществ это морфолин, пиперидин и аллиламин.

Из растворителей самым подходящим является водный раствор эмульгатора, менее пригодным метанол и наименее действенной вода.

Дискутируется и механизм возникновения инициационной системы, как и собственной инициации полимеризации.

Carbon tetrachloride has been known for a longer time as a chain transfer in radical polymerization reactions. In recent years it has also attracted attention as

a component of initiation systems, mainly with amino alcohols and salts of copper, iron, and other transition metals [1—11] and in the presence of water. Instead of amino alcohols, ammonium hydroxide [5], cellulose [12—16], starch [17], and polyamide-6 [18] can be used. In all cases a salt of transition metal is a necessary part of the initiation system. In spite of this, we have found out [19] that oxygenous or nitrogenous organic compounds (with lone electron pairs on oxygen or nitrogen) together with polyhalogenalkanes (mainly carbon tetrachloride) and water form an initiation system suitable for the polymerization of vinyl monomers.

The influence of individual components of the initiation system, in the absence of salts of transition metals, on the emulsion polymerization of vinyl chloride was studied in this work.

Experimental

Chemicals

Vinyl chloride (VC) (CHZWP Nováky) — freshly distilled prior to use; cont. (in p.p.m.) 0.5 acetylene; 1.5 1,1-dichloroethylene; 5.0 trans-1,2-dichloroethylene; 12.0 cis-1,2-dichloroethylene; 7.0 dichloroethane and 1.0 acetaldehyde.

Sodium laurylsulfate (purity 99.2% (wt)).

Alkali cellulose (Chemosvit, Svit) — prepared from purified wood pulp Carbicel S-20 and sodium hydroxide; contd. 34.27% (wt) of α-cellulose and 14.07% (wt) of sodium hydroxide.

Carbon tetrachloride (Lachema, Brno) — reagent grade purity contd. free chlorides of 1×10^{-4} % (wt).

"Spent liquor" obtained from alkali cellulose production, or waste alkali obtained after dialysis (Chemosvit, Svit), concentration of hemicelluloses 1.8% (wt); conc NaOH 1.36% (wt).

n-Butyr-di-n-butylacetal — b.p. 105—106°C/2 kPa; $n_D^{20} = 1.4211$.

Water — redistilled.

Sulfate lignin (Severoslovenské celulózky a papierne, Ružomberok) — dry-material cont. 85.5% (wt).

n-Butyraldehyde — fraction b.p. 74°C/99.3 kPa; $\varrho_{20} = 817$ kg m^{-3}; $n_D^{20} = 1.3842$.

Morpholine — freshly rectified before use, b.p. 127.9—128.3°C/101.3 kPa; $\varrho_{20} = 1004.3$ kg m^{-3}; $n_D^{20} = 1.4547$.

Trioxan — m.p. 62—62.5°C; b.p. 114.5°C/101.2 kPa; $\varrho_{65} = 1173$ kg m^{-3}.

The other compounds employed were of reagent grade purity.

Procedure

The experiments were carried out in glass ampules of 100 cm^3 volume provided with a special seal. Each ampule contained aqueous solution of sodium laurylsulfate (40 g, conc

1% (wt)), polyhalogenalkane, usually carbon tetrachloride (3 g) and oxygen- or nitrogen-containing organic compound (2 g). After sealing and deaeration of the ampule, vinyl chloride was added (20 g). Further, 6 ampules were fastened on a special shaft and immersed into a thermostated water-bath containing 10% (wt) of ethylene glycol. Rotation of the shaft was switched on (60 r.p.m.) causing agitation of ampules. The time of immersing the ampules into the bath and the commencement of rotation was considered the zero time. Temperature was controlled for ±0.1°C. The experiments were interrupted by pulling out the ampules, immersing them into cold water, and degassing unpolymerized VC. The emulsion in the ampules was quantitatively transformed into beakers and coagulated by means of aqueous solution of sodium chloride or by diluted hydrochloric acid.

The suspension of PVC was filtered off, thoroughly washed in warm distilled water until the test for chloride ions showed a negative reaction. The product of emulsion PVC was then dried at 50—55°C *in vacuo*. From the weight of the product the conversion of VC and yield of emulsion PVC was calculated. In several experiments, K values and the specific viscosity of isolated PVC were estimated. The curves were expressed by means of empirical equations following the Strejs method on the microcalculator Hewlett—Packard 9830.

Results and discussion

A survey of results on the influence of certain oxygen-containing organic compounds as the components of the initiation system carbon tetrachloride——oxygenous organic compound on the emulsion polymerization of VC in isochronous experiments (12 h) at 60°C is given in Table 1.

From these experiments it follows that favourable results in addition to alkali cellulose were achieved mainly with lignin and particularly owing to the presence of sodium hydroxide, with hemicelluloses, paraldehyde, ascorbic acid, n-butyr-di-n--butylacetal, ethylene oxide, and sucrose. With trioxan and sucrose alone, and without the addition of oxygenous organic compound the VC polymerization practically fails to proceed.

In Table 2 the solvents used are compared. The best results were obtained when using aqueous solution of emulsifier (sodium laurylsulfate) apparently also due to perfect contact of the reacting components achieved by emulsification. In the case of water itself, polymerization practically does not proceed particularly due to insolubility of carbon tetrachloride and VC in water. Better results were achieved in methanol, but the yields were only half in comparison with those achieved in the case of the emulsifier (sodium laurylsulfate). A possible explanation for this fact can be given mainly by the lower solubility of alkali cellulose in methanol. It cannot be either excluded that water or another polar compound also forms a part of the actual initiation system. In such a case larger polarity of water in comparison with methanol can form a faster or a more efficient initiation system.

Table 1

Effect of the oxygenous organic compounds as components of the initiation system (CCl_4—oxygenous organic compound) on the emulsion polymerization of VC at $60 \pm 0.1°C$

Charge to 100 cm^3 ampule: 40 g aqueous solution of sodium laurylsulfate; 1% (wt) conc, 3 g CCl_4, x g oxygenous organic compounds, 20 g VC; duration of experiments 12 h

Oxygen-containing organic compound		Yield PVC %	K Value
Type	Amount g		
	0	1.5	—
Alkali cellulose	2	99.5	—
Alkali cellulose	2	99.3	49.1
Lignin + NaOH	2 + 1	100	46.0
Lignin	2	50.2	53.5
Hemicelluloses + NaOH	2 + 1	50.3	31
Paraldehyde	2	75	47.4
Paraldehyde	2	63	—
Trioxan	2	0	—
Ascorbic acid	2	50.4	34.5
Dioxan	2	92	—
n-Butyraldehyde	2	24	32
n-Butyr-di-n-butylacetal	2	99.5	35
Sucrose + NaOH	2 + 1	65.7	55.4
Sucrose	2	0.1	—
Ethylene oxide	2	86.5	50.8
Propylene oxide	2	46	—
Dibutyl ether	2	10	—
Glucose	2	10.6	—

In Table 3 the results of application of various polyhalogenhydrocarbons were again compared. The highest yields were unambiguously achieved with carbon tetrachloride. Without carbon tetrachloride and alkali cellulose (thermal polymerization) after 12 h at 60°C max. 3% (wt) yields of emulsion PVC were collected.

The best results with carbon tetrachloride are connected with lower strength of Cl_3C—Cl bond energy which is 284.6 kJ mol^{-1} whereas in the case of chloroform HCl_2C—Cl is 314.0 kJ mol^{-1} and with tetrachloroethane Cl_2CH—CH(Cl)—Cl is already 330.7 kJ mol^{-1} [20, 21]. Similarly, good results we have achieved [19] also in the emulsion polymerization of methyl methacrylate and styrene.

Consequently, the influence of the amount of carbon tetrachloride as a part of the initiation system CCl_4—alkali cellulose—H_2O was more carefully examined.

Table 2

Effect of solvents on the polymerization of VC initiated by CCl_4—alkali cellulose system at $60 \pm 0.1°C$
Charge to 100 cm^3 ampule: 40 g solvent, 3 g CCl_4, 2 g alkali cellulose, 20 g VC

Duration of experiment	Solvents		Yield PVC %	K Value
	Type	Amount g		
12	Aqueous solution of sodium laurylsulfate conc 1% (wt)	40	99.5	49.3
12	H_2O	40	7.8	—
12	H_2O	40	10	—
12	CH_3OH	40	52	52.7
12	CH_3OH	40	45	47

Table 3

Effect of polyhalogenalkane on efficiency of the initiation system polyhalogenalkane—alkali cellulose in the emulsion polymerization of VC at $60 \pm 0.1°C$
Charge to 100 cm^3 ampule: 40 g aqueous solution of sodium laurylsulfate, 1% (wt) conc, 2 g alkali cellulose, 20 g VC, x g polyhalogenalkane

Duration of experiment h	Alkali cellulose g	Polyhalogenalkane		Yield PVC %	K Value
		Type	Amount g		
12	2	CCl_4	3	99.5	51.2
12	2	$CHCl_3$	3.2	19.5	50.3
12	2	$Cl_2CHCHCl_2$	3.2	4	—
12	2	$Cl_2C=CCl_2$	3.2	4.2	—
12	0	—	0	0	—
12	0	—	0	3	—
12*	0	CCl_4*	3	7.6	—

* *Note:* 1 g NaOH added to the reaction system.

The emulsion polymerizations of VC were carried out at $60 \pm 0.1°C$ (Fig. 1) isochronously (12 h). The conversion of VC and the yields of emulsion PVC and its K values were evaluated from the dependence on alkali cellulose amount (Fig. 2).

The results given in Fig. 1 show not only increase in both conversion of VC and yields of emulsion type PVC with increasing content of carbon tetrachloride up to 5% (wt)/VC but also permanent decrease of K values of prepared PVC samples with rising carbon tetrachloride content in the polymerization system.
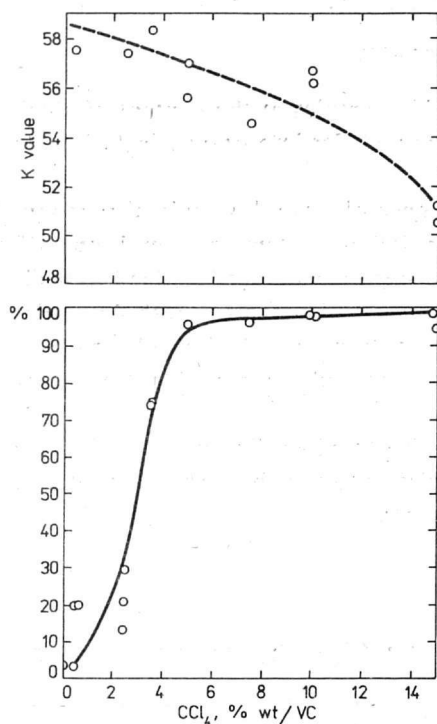
70

Fig. 1. Effect of carbon tetrachloride in the initiation system (CCl_4—alkali cellulose—H_2O) on VC conversion and the yield of PVC and its K values in isochronous experiments (12 h) at $60 \pm 0.1°C$.
Charge into ampules: 40 g aqueous solution of sodium laurylsulfate 1% (wt) conc; 20 g VC; 2 g alkali cellulose; x g CCl_4.
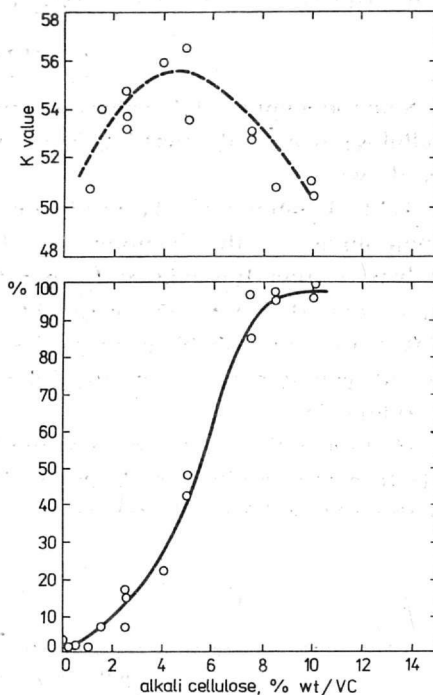
Fig. 2. Effect of alkali cellulose amount on VC conversion and K value in isochronous experiments (12 h) of emulsion polymerization at $60 \pm 0.1°C$.
Charge into ampules: 40 g aqueous solution of sodium laurylsulfate 1% (wt) conc; 20 g VC; 3 g CCl_4; x g alkali cellulose.

The dependence of vinyl chloride conversion P (in %) on the concentration of carbon tetrachloride x_c (in % wt, CCl_4/VC) at $60 \pm 0.1°C$ in the presence of 10% (wt) alkali cellulose/VC can be expressed by empirical equation

$$P = 100 \left\{ 1 - e^{-2x_c} \left[1 + 2x_c + 2x_c^2 + \frac{4}{3}x_c^3 + \frac{2}{3}x_c^4 + \frac{4}{15}x_c^5 \right] \right\}$$

In the case of the influence of alkali cellulose amount and the constant content of carbon tetrachloride (15% wt/VC) for the dependence of VC conversion on the concentration of alkali cellulose x_A (in % wt/VC) empirical equation was obtained

$$P = 100 \{1 - e^{-1.438x_A} [1 + 1.438x_A + 1.034x_A^2 + 0.496x_A^3 + 0.178x_A^4 + 0.081x_A^5 +$$
$$+ 0.012x_A^6 + 0.002x_A^7]\}$$

Some maximum of K values of emulsion PVC samples at the content of alkali cellulose around 4% (wt)/VC is not marked enough for important conclusions to be drawn.

Table 4 summarizes the results on the influence of several organic nitrogenous compounds as the components of the initiation system of emulsion VC polymerization. It is evident that pyridine and γ-picoline are nearly effectless while more remarkable results were obtained with piperidine and morpholine. The differences are probably connected with a greater strength of the lone electron pair on nitrogen in pyridine and γ-picoline owing to marked "aromatic" nature of the pyridine ring.

Hydrogenation of these compounds gives rise to piperidine with much loner electron pair on nitrogen. A similar situation also occurs in the case of morpholine with additional lone electron pairs on the oxygen.

Table 4

Effect of nitrogenous organic compounds in the initiation system (CCl_4—nitrogenous organic compound) on the emulsion polymerization of VC

Charge: 40 g aqueous solution of sodium laurylsulfate, 1% (wt), 3 g CCl_4, x g nitrogenous organic compound, 20 g VC; duration of experiments 12 h

Nitrogen-containing organic compound		Yield PVC %	K Value	Specific viscosity η
Type	Amount g			
Pyridine	2	10.4	—	—
Pyridine	2	16.4	—	—
Pyperidine	2	56.5	32	0.140
γ-Picoline	2	8	—	—
γ-Picoline	2	8	—	—
Allylamine	2	31.3	—	—
Morpholine	2	53.0	44.7	0.244

Owing to this we also investigated the influence of temperature on the emulsion polymerization of VC with morpholine-containing initiation system (CCl_4—morpholine—H_2O). The results are summarized in Table 5. The efficiency of this initiation system markedly decreases below 45°C.

We suppose in our case that at least the primary initiation of polymerization proceeds by a molecular-radical mechanism and further elemental steps probably

Table 5

Effect of temperature on the emulsion polymerization of VC

Charge: 40 g aqueous solution of sodium laurylsulfate, 1% (wt), 3 g CCl₄, 2 g morpholine, 20 g VC

Duration of experiment h	Temperature °C	Yield PVC %	K Value	Specific viscosity η
4	45	9.4	—	—
8	45	12.6	—	—
12	45	19.4	49.3	0.295
12	60	53.0	44.7	0.244
2	80	1	—	—
4	80	10	38.4	0.183
6	80	15.3	30.3	0.119
10	80	26.2	38.7	0.189
12	80	68.5	29.0	0.110

follow radical mechanism. In the stage of initiation probably a complex is formed between oxygenous or nitrogenous organic compound and polyhalogenalkane (particularly carbon tetrachloride) or monomer. The lone electron pairs on the oxygen or nitrogen weaken the strength of the C—Cl bond in the present polyhalogenalkane. In this way acts also the water in the system due to the lone electron pairs on the oxygen. Thus by using carbon tetrachloride trichloromethyl or chlorine radical can be easily formed, in contrast to the statements of other authors [1—4, 6—11] also in the absence of the salts of transition metals. The radicals then initiate easily VC polymerization.

Even though we suppose the molecular-radical mechanism of initiation of the polymerization by this initiation system, we cannot quite eliminate even molecular-ionic or ionic mechanism in which the initiation effect of trichlorocarbene $Cl_3C|$ or $Cl_3C^{(-)}$ would play an important role. This conception is partly supported both by information [22] that the mixture of carbon tetrachloride with sodium is capable to explode and is sensitive to shock and some data [22] on the existence of carbenes.

Our visualization on the molecular-radical mechanism of this polymerization is supported also by information [23] that carbon tetrachloride is able to form complexes with olefins and by our finding that some typical radical polymerization inhibitors and oxygen inhibit emulsion polymerization of vinyl chloride initiated by the system alkali cellulose—carbon tetrachloride—water. Accordingly while at $60 \pm 0.1°C$ in the presence of 10% (wt) alkali cellulose and 15% (wt) carbon tetrachloride (on vinyl chloride) without oxygen after 10 h of reaction 77% conversion was attained, at the overpressure of oxygen 0.1 MPa only 3%. The

polymerization is retarded by hydroquinone and dinitrobenzene, less by phenol (at 50°C during 5 h in the presence of 10% wt alkali cellulose and 15% wt CCl₄/VC with increasing content of phenol from 0 to 10% wt/VC by emulsion polymerization the yield of PVC dropped from 55 to 23%) and xylenols and no effect is exerted by copper salts.

The new initiation system carbon tetrachloride—oxygenous or nitrogenous organic compound—water, is interesting for the time being especially from the theoretical and partially from practical point of view for emulsion polymerization of vinyl chloride and other monomers. PVC prepared by this procedure, in spite of low K values shows, in comparison with polymers prepared by other initiation systems, higher thermal stability.

As oxygenous organic components of the initiation system, technically easily accessible materials e.g. hemicelluloses ("spent liquor") and other little utilized products may be applied.

Of interest may be application of the above-discussed systems in other syntheses.

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