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POLYMERIZATION OF BIS(2-CHLOROETHYL) VINYLPHOSPHONATE

Polimerizatsiya di- β , β' -khloretilovogo efira
vinilfosfinovoy kisloty)

by

V.A. Orlov, O.G. Tarakanov

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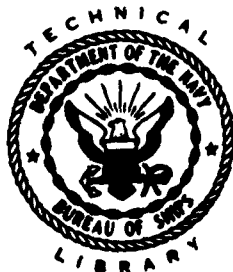
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POLYMERIZATION OF BIS(2-CHLOROETHYL) VINYLPHOSPHONATE

V. A. Orlov, O. G. Tarakanov

Bis(2-chloroethyl) vinylphosphonate (BCVP), $\text{CH}_2 = \text{CHP}(\text{O})(\text{OC}_2\text{H}_4\text{Cl})_2$ is a monomer capable of polymerizing. It is of considerable interest as an additive conferring fire resistance upon various polymerizing systems¹.

Furthermore, BCVP raises the resistance in the tropics of plastics based on polyvinyl chloride².

The object of this work was the study of the kinetics of the block polymerization of DCVP.

Middle fractions of the vacuum-distilled ester (B. P. 140⁰–143⁰ at p = 2–3 mm Hg, $d_4^{19} = 1.3196$, $n_D^{19} = 1.4780$) and freshly purified initiators were used in the polymerization study.

The rate of polymerization was determined dilatometrically by using the apparatus and procedure similar to those described in ref. 3, 4

The initiators employed were benzoyl peroxide (BP), azoisobutyrodinitrile (BDN), isopropylbenzene hydroperoxide (IBH), lauryl peroxide (LP) and tertbutyl peroxide (TBP).

The characteristic curve of the volume of BCVP versus the time of polymerization is given in Fig. 1.

As we know, the decrease in the volume of a polymerizing system is directly proportional to the extent of conversion of the monomer into a polymer⁵:

$$P = K\Delta V$$

where P is the degree of polymerization, %

ΔV is the volume decrease of the polymerizing system, % of initial;

K is the proportionality constant.

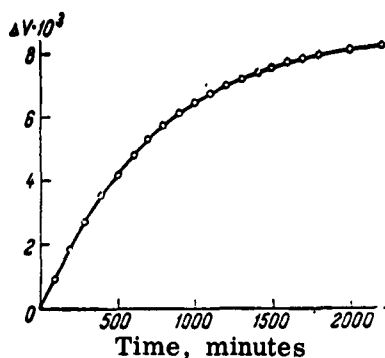


Fig. 1. Decrease in the volume of BCVP (ΔV) versus the time of polymerization ($t = 70^\circ$, concentration of BP, 2%).

We did not set up any special experiments for the exact determination of constant K , but at the end of each experiment we separated the polymer formed from the monomer. Owing to the low molecular weight of the polymer and the high boiling range of BCVP, it is difficult to separate these two substances. The value of K calculated from the yield of the polymer was found to be approximately equal to eight.

The maximum yield of the polymer obtained in the presence of the initiators mentioned above amounted to 70 – 85%.

As shown in Fig. 1, the rate of polymerization of BCVP is constant in the beginning, but begins to drop after a certain degree of conversion has been reached. No acceleration of polymerization, characteristic of systems exhibiting the gel effect, was observed with BCVP.

To explain the effect of air on the polymerization of the monomer, the process was carried out in two ampoules simultaneously; the monomer in one ampoule was thoroughly deaerated and the ampoule was sealed under vacuum, while the air was not removed from the second ampoule and the latter was not sealed. It was found that the polymerization of the monomer takes place a little faster in the presence of air.

Below, we give the data on the initial rates of polymerization of BCVP, which were determined from the initial linear segments of curves similar to the curve of Fig. 1.

Depending on the conditions of the experiment, the polymerization of DCVP in the presence of the enumerated initiators proceeds up to the formation of a viscous, resinous mass, or to the appearance of a yellow, insoluble, elastic product. By successive reprecipitations from a solution of the resinous mass in acetone, we were able to extract, using ethyl ether, a polymer which, after drying under vacuum, appeared as a brittle and very hygroscopic white substance. The polymer was soluble in ordinary polar organic solvents. The molecular weight, measured by the method of the boiling-point elevation, was found to be 2700. The molecular weight of the polymer separated from the mixture which had polymerized at 5–8% conversion was found to be 1200.

We tried to fractionate the resinous mass obtained from the polymerization of DCVP after 21 hours at 110° in the presence of 4.44%wt. TBP. The fractionation was performed by precipitating the polymer with ethyl ether from its solution in acetone (Table 1).

Table 1
Composition of Fractions from the Resinous Mass of BCVP

Fractions	Relative wt., %	Spec. viscos. of 5% solutions in acetone	Mol. wt. of frac.
—	—	0,058*	—
1	40,6	0,096	1900
2	30,8	0,153	3200
3	15,4	0,234	—
4	13,2	0,335	6000

*Specific viscosity of a 5% solution of the monomer in acetone

The specific viscosity was determined with a suspended-level viscometer for a time of flow of the solvent of 120 seconds.

A thermomechanical curve plotted for a repeatedly reprecipitated polymer of DCVP with the use of a Kargin balance for a load of 0.280 kg/cm² is shown in Fig. 2. The softening temperature of the polymer determined from this curve $\approx 50^{\circ}$.

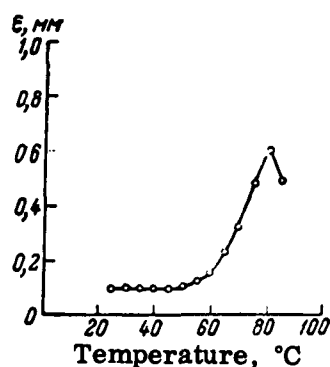


Fig. 2. Thermomechanical curve for a repeatedly reprecipitated polymer of BCVP.

The initial polymerization rates, $\nu_{in.}$, in percent decrease of the volume of the polymerizing system per minute in the presence of initiators at 60°, are given in Table 2.

Table 2

Initial polymerization rates of BCVP ($t = 60^\circ$)

Initiator concentration *	Initial rate, $v_{in} \times 10^3$									
	BDN		BP		IBH		LP		TEP*	
	+a	-a	+a	-a	+a	-a	+a	-a	+a	-a
0.2 wt. %	3.35	3.11	1.56	1.17	1.12	1.04	—	—	—	—
0.282 mole %	3.35	3.11	3.08	2.55	Long induction period	0.715	7.15	—	0.25	0.6

*Data for 80° .

Note: +a — monomer from which air had not been removed; -a — deaerated monomer.

The polymerization of BCVP with BDN as the initiator was studied more thoroughly. Curves showing the dependence of the polymerization rate on the temperature and the concentration of BDN (Fig. 3 and 4) were plotted from the results of these experiments.

The polymerization was carried out in the absence of air.

The straight line (Fig. 3) is given by the following equation:

$$\log v_{in} = -\frac{6640}{T} + 17.456 \quad (1)$$

where T is the absolute temperature.

The total activation energy of the polymerization of BCVP, calculated from the data cited, is equal to 30.4 kcal/mole.

It is apparent from Fig. 4 that the initial polymerization of BCVP from which air had not been removed shows a linear variation with the square root of the BDN concentration in the range of concentrations from 0.2 to 1.0 wt. %. The straight line is given by the following equation:

$$v_{in} = 0.105\sqrt{C} - 0.00198 \quad (2)$$

where C is the concentration of the BDN initiator expressed in mole fractions.

It should be noted that even small amounts of water affect the polymerization rate of BCVP considerably. For instance, in the presence of 0.1–0.7% water, the rate decreases several times.

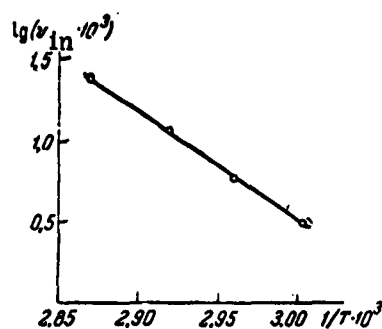


Fig. 3. Polymerization rate of BCVP versus temperature (BDN concentration, 0.2%)

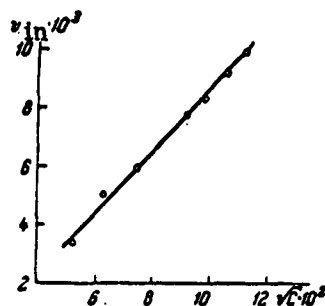
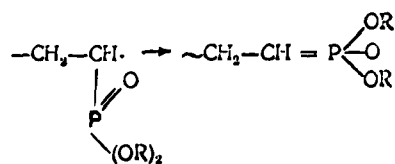


Fig. 4. Polymerization rate of BCVP versus the concentration C of BDN in mole fractions ($t = 60^\circ$).

It is known from the literature^{6,7} that polymers of vinylphosphonic esters have a molecular weight of 2000 to 7000 and that their polymerization occurs only in the presence of initiators.

The results we obtained agree with these data. The low molecular weight of the DCVP polymer allows one to assume a high rate of breaking of the growing chain. The results of the fractionation indicate that the proportion of the low-molecular fraction is appreciable.

Arcus and Matthews suggested that the breaking of the growing chains takes place as a result of the formation of a stable radical in the rearrangement of the end of the growing chain, as follows:



(3)

It is possible that the stable radical is formed in the interaction between a growing radical and —OR groups⁷. However, both hypotheses concerning the reaction mechanism require experimental evidence.

CONCLUSIONS

1. The block polymerization of bis(2-chloroethyl)vinylphosphonate in the presence of various initiators was investigated.
2. A plot was made of the variation of the initial rate of polymerization with the temperature, and with the concentration of azoisobutyrodinitrile. The total activation energy for the polymerization of BCVP was calculated.
3. The dependence of the polymerization rate of BCVP on the presence of atmospheric oxygen and humidity was demonstrated.
4. The molecular weights of the polymers of BCVP were determined.

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