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Abstract

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THE EFFECT OF PERCHLORATE SALTS ON THE POLYMERIZATION OF STYRENE

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CHEMISTRY

The polymerization of ethylene derivatives is strongly affected by any impurities: some of them accelerate polymerization, while others, on the contrary, inhibit it, increasing the induction period ([1,2]).

For our work we required large quantities of styrene containing minimal amounts of moisture. As a drying agent we chose anhydrous magnesium perchlorate (“anhydrone”), proposed in 1922 by Willard and Smith ([3]) as a desiccating agent. However, polystyrene was found in styrene that had stood over anhydrous magnesium perchlorate at 10°. The polymerizing ability of magnesium perchlorate was discovered by Chilly and Foster ([4]), who also used it for drying styrene.

We decided to verify this fact and to determine the effect of several other perchlorates (barium, potassium, and ammonium) on the polymerization of styrene.

Experimental part

At first the polymerization was carried out in sealed ampoules. Styrene, washed with alkali and distilled water and then thoroughly dried, was distilled in vacuum.

The fractionated styrene was again distilled in vacuum into ampoules into which equal weighed amounts of magnesium, barium, or potassium perchlorate had previously been placed.

Before use, the perchlorates were twice recrystallized from aqueous solutions, suction-filtered on glass filters, and the crystalline hydrates were dehydrated under vacuum at about 0.1 mm Hg.

The sealed ampoules were placed in a thermostat heated to 80°; every hour from the start of the experiment an ampoule was removed from the thermostat, opened, and analyzed for polymer content by the refractive index. To determine the content of polystyrene in styrene from the refractive index, we used the method of an empirical calibration curve ([5]) (see Fig. 1).

The contents of the ampoule were dissolved in benzene, and methyl alcohol was added to the benzene solution with vigorous stirring. The precipitated

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white flakes of polystyrene were washed several times with methyl alcohol and dried under vacuum to constant weight. The average molecular weight of the polystyrene was determined viscometrically from the viscosity of the benzene solution.

Fig. 1. Calibration curve for solutions of polystyrene in styrene:
I —experimental data; *II* —calculated data.

The very first experiments showed that perchlorates shorten the induction period and accelerate the polymerization of styrene.

However, polymerization in ampoules with different amounts of perchlorates showed no dependence between the polymerization rate and the amount of perchlorates in the polymerization mixture.

We assumed that the formation of the initial active centers occurs on the surface of the perchlorates, i.e., heterogeneously.

Proceeding from this assumption, it becomes clear why, with different amounts of perchlorates, the same polymerizing capacity is observed: perchlorates are almost insoluble in styrene and, in any amount, lie at the bottom of the ampoule as a dense layer, having approximately the same surface of contact with the styrene.

Fig. 2. Kinetics of styrene polymerization in the presence of magnesium perchlorate at 80°:
I —pure styrene, *II* —$0.25 \cdot 10^{-2}$, *III* —$0.5 \cdot 10^{-2}$, *IV* —$1.0 \cdot 10^{-2}$

Fig. 3. Dependence of the rate of styrene polymerization in the presence of magnesium perchlorate (*a*) on temperature, *b* —polymerization of pure styrene; *I* —70°, *II* —80°, *III* —90°

Therefore, in the subsequent work we used the method described by Shostakovskii, Shishkov, and Neterman (6).

Polymerization was carried out in a stream of inert gas in a reaction vessel equipped with a stirrer, reflux condenser, thermometer, and a side arm for sampling.

The kinetic curve was obtained as follows.

At definite time intervals after the beginning of heating, a sample (0.2 ml) of the styrene + perchlorate mixture was taken from the reaction vessel, transferred to a centrifuge tube, and freed from perchlorate by centrifugation.

Then the refractive index n_D^{20} of the solution above the precipitate was determined, and the polymer yield was determined from a calibration curve.

The polymer was precipitated from the solution with methyl alcohol; the viscosity was determined in benzene solution.

The experimental data showed that perchlorates not only shorten the induction period, but also increase the polymerization rate. Polymerization with stirring showed that, as the amount of perchlorates in the polymerization mixture increases, the polymerization rate increases (Figs. 2, 3).

At the initial stage of styrene polymerization in the presence of potassium, barium, and ammonium perchlorates, the rate proved to be directly proportional to the monomer concentration and to the catalyst concentration.

The overall rate of polymerization in this case is described by the equation:

$$w_n = K[M][C] + \beta[M],$$

where K is a rate constant depending on the catalyst; β is a constant

rate of thermal polymerization; $[M]$ is the concentration of styrene, mol/l; $[C]$ is the concentration of perchlorate, mol/l; or

$$\frac{dM}{d\tau} = K[M][C] + \beta[M].$$

For potassium perchlorate at 80° the value of K proved to be $11.5 \cdot 10^{-4}$ l/mol • min, for ammonium perchlorate $9.86 \cdot 10^{-4}$, for barium perchlorate $5.2 \cdot 10^{-4}$, and for magnesium perchlorate $3.56 \cdot 10^{-2}$ l/mol • min.

In the presence of magnesium perchlorate, the polymerization of styrene proceeded at a rate greatly exceeding the rate of polymerization in the presence of other perchlorates. The dependence of the polymerization rate on the concentration of magnesium perchlorate proved to be different from that observed with the other perchlorates.

The temperature coefficient was found to be 1.6 in the case of potassium and ammonium perchlorates, 2.56 for barium perchlorate, and 1.15 for magnesium perchlorate. The activation energy of styrene polymerization in the presence of perchlorates was determined graphically (Fig. 4); it proved to be lower than the activation energy of the thermal polymerization of styrene in the absence of perchlorates: for $KClO_4$, 11,730 cal/mol; for NH_4ClO_4, 14,300 cal/mol; for $Ba(ClO_4)_2$, 14,870 cal/mol.

With an increase in the amount of perchlorates in the polymerization mixture, the molecular weight of the polymer obtained decreases. The polymerization of styrene in the presence of perchlorates has a chain mechanism.

Analysis of the polymer showed that it consists entirely of carbon and hydrogen, corresponding to the formula $(C_3H_8)_n$ (the elemental composition of the polymer was determined and the absorption spectra of polystyrene films in the infrared region were studied).

Decomposition of potassium, barium, and magnesium perchlorates in styrene does not occur in the temperature range studied by us (20–90°).

Fig. 4. Kinetics of the polymerization of styrene in the presence of potassium perchlorate at 80°:
I –polymerization of pure styrene; *II* –perchlorate concentration $0.5 \cdot 10^{-2}$ mol per 1 mol of styrene; *III* –$1 \cdot 10^{-2}$ mol per 1 mol of styrene; *IV* –$2 \cdot 10^{-2}$ mol per 1 mol of styrene.

The study of the effect of potassium, barium, and magnesium chlorides on the polymerization of styrene showed that all of them increase the induction period and are inhibitors.

It follows from the foregoing that, in the case of the use of potassium and barium perchlorates, so-called heterogeneous-homogeneous catalysis evidently takes place, i.e., the formation of active centers occurs on the surface of the perchlorate with formation of a complex, while the growth of macromolecules occurs in the bulk of the monomer, i.e., homogeneously.

Magnesium perchlorate is a stronger catalyst than the other perchlorates used by us. Here, apparently, in addition to heterogeneous catalysis, ionic polymerization also takes place: the polymerization of styrene proceeds, although slowly, even at comparatively low temperatures; the temperature coefficient of the reaction is small (1.15); the molecular weight of polymers obtained in the presence of magnesium perchlorate is low and almost does not depend on the amount of perchlorate. The independence of the molecular weight of the polymer from the amount of magnesium perchlorate indicates the absence in this process of the recombination mechanism of chain termination characteristic of radical polymerization.

The action of magnesium perchlorate on the polymerization reaction of styrene, differing from the action of the other perchlorates, may be due to its

excessive hygroscopicity. We cannot guarantee the absolute absence of traces of moisture in anhydrone.

S. S. Medvedev (7), as well as Evans and Polanyi (8), believe that traces of moisture are sufficient to initiate ionic polymerization. In addition, it is known that perchlorates may contain traces of perchloric acid, from which it is very difficult to free them.

In both cases, the initiator of polymerization may be the hydrogen ion H^+, and polymerization may proceed by the so-called carbonium mechanism.

Table 1

Molecular weights of polystyrenes obtained in the presence of perchlorates at 80°

No.	Perchlorate	Amount of perchlorate, mol per 1 mol styrene	Molecular weight of polymer (M)	Degree of polymerization (n)
1	–	–	184000	1770
2	Potassium perchlorate	$0.5 \cdot 10^{-2}$	168250	1618
3	Potassium perchlorate	$1.0 \cdot 10^{-2}$	158260	1522
4	Potassium perchlorate	$2.0 \cdot 10^{-2}$	143210	1377
5	Ammonium perchlorate	$0.5 \cdot 10^{-2}$	129510	1245
6	Ammonium perchlorate	$1.0 \cdot 10^{-2}$	106540	1024
7	Ammonium perchlorate	$2.0 \cdot 10^{-2}$	107680	1035
8	Barium perchlorate	$0.5 \cdot 10^{-2}$	125920	1211
9	Barium perchlorate	$1.0 \cdot 10^{-2}$	117450	1129
10	Barium perchlorate	$2.0 \cdot 10^{-2}$	109030	1048
11	Magnesium perchlorate	$0.125 \cdot 10^{-2}$	9620	92
12	Magnesium perchlorate	$0.25 \cdot 10^{-2}$	10050	96

No.	Perchlorate	Amount of perchlorate, mol per 1 mol styrene	Molecular weight of polymer (M)	Degree of polymerization (n)
13	Magnesium perchlorate	$0.5 \cdot 10^{-2}$	10890	104
14	Magnesium perchlorate	$1.0 \cdot 10^{-2}$	3060	30

The authors consider the proposed mechanism neither rigorously proven nor unambiguous.

Conclusions. 1. The effect of potassium, ammonium, barium, and magnesium perchlorates on the polymerization of styrene at 20, 40, 70, 80, and 90° was investigated. It was found that the above-mentioned perchlorates are catalysts of the polymerization reaction of styrene.

2. In studying the kinetics of styrene polymerization in the presence of potassium, ammonium, and barium perchlorates, it was established that the rate of the process is satisfactorily described by the equation:

$$\frac{dM}{d\tau} = K_1[M][C] + \beta[M].$$

3. In the case of potassium and barium perchlorates, apparently, so-called heterogeneous-homogeneous catalysis takes place.

4. When magnesium perchlorate is used, the rate of polymerization is proportional to the concentration of magnesium perchlorate when its content is greater than 0.125 mol/mol of styrene.

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