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Physical Chemistry

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Abstract

Full Text

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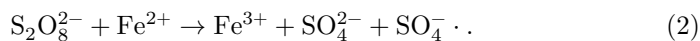
APPLICATION OF ELECTROCHEMICAL REDUCTION OF PERSULFATE TO INITIATE A POLYMERIZATION REACTION

(Presented by Academician A. N. Frumkin, June 21, 1962)

It is known that persulfate is widely used to initiate polymerization reactions (^{1,2}). The use of persulfate is based on its ability to form free radicals $\text{SO}_4^- \cdot$ upon thermal decomposition (³):

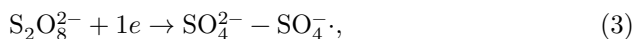


by means of oxidation-reduction reactions (^{4,5}):



Oxidation-reduction systems are more controllable and make it possible, to some extent, to regulate the rate of initiation (⁶).

From our point of view, a much more flexible and controllable system for initiating polymerization can be created on the basis of the electrochemical properties of persulfate. It is known that persulfate is reduced on mercury (⁷) and platinum (⁸) electrodes. Moreover, there is an assumption (⁷), based on the shape of the polarographic curve, that the process of persulfate reduction at the electrode proceeds stepwise, although there is no exact proof of this. If this assumption is accepted as correct, then the first stage of the process should be:



i.e., upon reduction of persulfate at the electrode, the radical $\text{SO}_4^- \cdot$ is obtained, which, as is known (⁹), is capable of initiating polymerization.

The possibility of such an assumption was tested in the polymerization of acrylamide. In the experiments, a 10% solution of acrylamide was used, such as is usually employed for its polymerization (⁹⁻¹¹); the concentration of potassium persulfate was 0.1%. Electrolysis was carried out on platinum, nickel, and amalgamated silver electrodes at room temperature (18—20°C). A control solution

Fig. 1. Dependence of the intrinsic viscosity of polyacrylamide (I) and the degree of polymerization (II) on current density

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of the same composition was kept for 24 hours; polymerization did not occur in it.

Electrolysis was carried out at such current densities that only reduction of persulfate occurred and, consequently, initiation of polymerization took place. Indeed, at current densities of 20—100 $\mu\text{a}/\text{cm}^2$ (Fig. 1), we were able to obtain quantitatively a fairly viscous polymer; moreover, the maximum viscosity and maximum depth of polymerization were reached at an optimal current density that was exactly the same for the different electrodes (platinum, nickel, amalgamated silver). At higher current densities, when the hydrogen-evolution potential was reached, practically no polymer was obtained. Evidently,

reduced hydrogen atoms do not take part in initiating polymerization. Although in our experiments oxygen was not removed from the solution, we could not attribute the initiation to oxygen reduction⁽¹⁵⁾, since when the persulfate in the solution was replaced by an equivalent amount of sulfate or sulfuric acid, no polymer was detected after electrolysis.

All quantitative measurements were carried out in glass cylindrical electrolyzers in which the cathode and anode spaces were separated by a diaphragm made of porous glass. It is interesting that in some cases (at minimum current densities) polymer was also obtained in the anode space. This also indicates that the initiation of polymerization occurs only upon reduction of persulfate, which, as is known, may also be possible at a positive potential.

Fig. 1. Dependence on current density of the intrinsic viscosity of polyacrylamide (I) and the degree of polymerization (II)

Polymerization proceeded for three hours, for which purpose continuous electrolysis was carried out at constant current density. Thereafter, the degree of polymerization was measured polarographically from the decrease in monomer⁽¹²⁾, and the intrinsic viscosity of the resulting polymer was also measured. The data presented (Fig. 1) show that the intrinsic viscosity and the degree of polymerization depend on the current density. Thus, the use of electrochemical initiation makes it possible, very simply and without changing the temperature or the initiator concentration, to regulate the rate of the process and thereby obtain the required polymer quality. At the optimum current density, the intrinsic viscosity of the polymer obtained in three hours of electrolysis is 4.3 at the maximum degree of polymerization. In quality this polymer is not inferior to polymer obtained in 24 hours at room temperature⁽¹³⁾, or in 14 hours with heating⁽¹⁰⁾.

The proposed method of electrochemical initiation of acrylamide polymerization not only makes it possible to obtain a polymer, but in practice is more advantageous than the known chemical methods of initiation. In addition, the very fact that polymer is obtained is proof of the assumption ⁽⁷⁾ that the persulfate ion is reduced at the electrode stepwise. Otherwise, initiation of polymerization would be impossible.

The principle of electrochemical initiation, based on the formation of free radicals during reduction of a peroxide compound at the electrode, can be applied not only to the polymerization of acrylamide but also to other polymerization reactions.

the electrode, can evidently be used for the polymerization of other substances ¹⁵, and can also be used for theoretical investigations, since it makes it possible to carry out initiation at a specified constant rate.

We express our gratitude to Academician A. N. Frumkin for the comments made during discussion of the work.

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