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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

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PHYSICAL CHEMISTRY

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PARTICIPATION OF THE EMULSIFIER IN REDOX INITIATION OF EMULSION POLYMERIZATION

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A number of authors [1,2] have established that one of the important factors affecting the kinetics of polymerization in emulsions is the nature of the emulsifying agent. The nature of the emulsifier used affects not only the rate of the polymerization process, but also, in a definite way, the properties of the polymers formed [3].

Such an effect of the emulsifier on the kinetics of the polymerization process in emulsions must be connected primarily with the purely colloid-chemical properties of the soaps used, namely: the critical micelle-formation concentration, the size and shape of the micelles, and the ability of the emulsifier micelles colloidally to dissolve the monomer and initiator, since the micelles of a surface-active emulsifier, as was shown earlier, are the site at which the polymerization process in emulsions occurs.

Fig. 1. Kinetics of polymerization of styrene in the presence of sodium carbonate. Concentration: Na_2CO_3 0.1 N, CPB 0.01 M (in the aqueous phase), IPH 0.01 M (in the hydrocarbon phase). 1 –60°; 2 –40°; 3 –4°; 4 –30°; 5 –18°

Fig. 2. Kinetics of polymerization of styrene. Concentrations: CPB 0.01 M (in the aqueous phase), IPH 0.01 M (in the hydrocarbon phase). 1 –20°; 2 –40°; 3 –60°

Fig. 3. Kinetics of HPI decomposition. Concentrations: HPI, CPB 0.01 M, Na2CO3 0.1 N (in aqueous solution), 1 –HPI, t = 100°; 2 –HPI + CPB, t = 100°; 3 –HPI + CPB + Na2CO3, t = 20°; 4 –HPI + CPB + Na2CO3, t = 50°

Figure 3: Fig. 3. Kinetics of HPI decomposition. Concentrations: HPI, CPB 0.01 M, Na2CO3 0.1 N (in aqueous solution), 1 –HPI, t = 100°; 2 –HPI + CPB, t = 100°; 3 –HPI + CPB + Na2CO3, t = 20°; 4 –HPI + CPB + Na2CO3, t = 50°

In studying emulsion polymerization in the presence of various emulsifiers, we observed a number of special features in the course of the polymerization process when cetylpyridinium bromide (CPB) was used. The experiments showed that in this case the role of the emulsifier cannot be reduced solely to a purely colloid-chemical factor.

The investigation was carried out by the dilatometric method in a dilatometer that excluded contact of the polymerization system with air [(4)]. Stirring was performed with a magnetic stirrer. All experiments were carried out at a hydrocarbon-to-aqueous phase ratio of 1:9. Isopropylbenzene hydroperoxide (IPH) was used as the initiator, and styrene as the monomer.

The kinetics of polymerization at different temperatures was studied. In one series of experiments, sodium carbonate was introduced into the aqueous phase in an amount-

in an amount of 0.1 g-eq per 1 l of the aqueous phase. The results of these experiments are presented in Fig. 1. As can be seen from the data given, the rate of the polymerization reaction is considerably higher than when other classes of emulsifiers are used (sulfomyol, salts of fatty acids) under otherwise equal conditions; CPB ensures an acceptable polymerization rate at reduced temperatures (4 and 18°), which does not occur in the presence of other emulsifiers. The most significant distinction of polymerization in the presence of CPB is that, in the presence of soda in the aqueous phase, the polymerization rate, as the temperature is raised, passes through a maximum.

It is interesting to note that in experiments carried out at 40 and 60°, polymerization develops at a certain rate in the initial stages, then rapidly slows down and soon ceases completely, which is naturally to be associated with exhaustion of the initiator. With lowering of the temperature, polymerization proceeds at a sufficient rate with a simultaneous increase in the yield of polymer.

In experiments carried out in the absence of soda, with increasing temperature a regular increase is observed in the rate of the polymerization process, while the linear dependence $S = f(t)$ is retained up to a considerable depth of polymerization (Fig. 2).

Fig. 3. Kinetics of HPI decomposition. Concentrations: HPI, CPB 0.01 M, Na_2CO_3 0.1 N (in aqueous solution), 1 –HPI, $t = 100°$; 2 –HPI + CPB, $t = 100°$;

3 –HPI + CPB + Na_2CO_3, $t = 20°$; 4 –HPI + CPB + Na_2CO_3, $t = 50°$.

As a result of comparing the kinetic data obtained in experiments with the introduction of sodium carbonate and without it, one may conclude that additions of soda and an increase in temperature act in the same direction—increasing the polymerization rate.

The rate of the polymerization process is determined by the rate of initiation, which, in turn, depends on the decomposition reaction of the initiator, the source of primary free radicals. However, with a sharp increase in the concentration of free radicals, owing to rapid decomposition of the initiator, a considerable portion of them is consumed unproductively, entering into recombination reactions. At the same time, as a result of accelerated decomposition of the initiator, it is exhausted already in the early stages of polymerization. As experiment shows, such accelerated decomposition of the initiator is caused by CPB.

The decomposition of HPI, used as the initiator, in aqueous solution is considerably accelerated upon the introduction of CPB even in the absence of Na_2CO_3. An even greater acceleration of HPI decomposition is observed in the case of the simultaneous presence of CPB and soda. Data on the kinetics of HPI decomposition under various conditions are presented in Fig. 3.

The considerable acceleration of HPI decomposition under the influence of CPB, which is absent when other emulsifiers are used, in our opinion is explained by an oxidation–reduction reaction occurring between HPI and CPB, this reaction proceeding more rapidly in the presence of soda. This point of view is confirmed by the fact that the polymerization of styrene in the presence of the oxidation–reduction initiating system HPI—pyrophosphate complex of ferrous iron is described by analogous regularities (Fig. 4).

An increase in temperature causes an increase in the initial rate of polymerization with a decrease in the final yield of polymer, i.e., with exhaustion of the initiating system at earlier stages of the polymerization process. The addition of sodium carbonate has the same effect.

It was established in separate experiments that the oxidation–reduction reaction in the GPI–$Fe^{\bullet\bullet}$ system is accelerated when the temperature is raised and when soda is added.

It appears probable that, in emulsion polymerization with the emulsifying and initiating agents indicated above, activation takes place as a result of hydrolytic cleavage of the pyridine ring in an alkaline medium ([5,6]):

$$\text{(I)} \xrightarrow[\text{alk. med.}]{\text{Br}^-} \text{(II)} \xrightarrow{\text{OH}^-} \text{(III)} \longrightarrow \text{(IV)} \rightleftharpoons \text{(V)}$$

The role of polymerization activators may be fulfilled both by the aldehyde group and by the > NH group ([7]), which are formed when the ring opens. The scheme given above is also supported by the fact that the final decomposition

Fig. 4. Kinetics of styrene polymerization in the presence of the oxidation–reduction initiating system GPI–pyrophosphate complex of ferrous iron.

Figure 4: Fig. 4. Kinetics of styrene polymerization in the presence of the oxidation-reduction initiating system GPI–pyrophosphate complex of ferrous iron.

products, as experiment shows, are colored yellow-orange, which should be the case for compounds IV and V, as derivatives of glutaconic aldehyde.

Fig. 4. Kinetics of styrene polymerization in the presence of the oxidation-reduction initiating system GPI–pyrophosphate complex of ferrous iron. Concentration of nekal in the aqueous phase 2%, concentration of GPI 0.03 M (in the hydrocarbon phase).
1 –temperature 5° in the presence of Na_2CO_3; 2 –5° without soda; 3 –15° without soda.

Comparison of the data presented makes it possible to conclude that a surface-active emulsifier (in the present case, cetylpyridinium bromide) can play a dual role in emulsion polymerization.

First, it can act as an ordinary emulsifier, stabilizing the initial monomer emulsion and the latex formed, and also ensuring the course of the polymerization process in the aqueous phase owing to the conjugated dissolution of the monomer and initiator.

Second, the emulsifier can exhibit the functions of a polymerization activator, causing induced decomposition of the hydroperoxide, which leads to a sharp increase in the rate of the polymerization process even at low temperatures, at which polymerization does not proceed under ordinary conditions.

By activating the decomposition of GPI as a result of the oxidation-reduction reaction, CPB accelerates the formation of primary free radicals, the initiation reaction, and consequently the entire polymerization process as a whole.

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named after Ivan Franko

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Note: Figure translations are in progress. See original paper for figures.