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Abstract

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EMULSION POLYMERIZATION WITH SURFACE-ACTIVATED INITIATION

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The production of polymers by polymerization in an emulsion stabilized by surface-active substances of the soap type ([1]), with the formation of latices, despite a number of advantages, encounters a number of difficulties associated with the isolation of the polymerizate, as well as with the impossibility of obtaining it in pure form.

In the search for new approaches, studies of bead polymerization have become widely developed; this is polymerization in bulk with effective cooling by water, with stabilization of the aqueous polymer emulsion by high-molecular colloidal electrolytes or inorganic salts. However, in bead polymerization it proved impossible to obtain polymers of high molecular weight at acceptable process rates.

We saw the paths toward solving this problem, first, in the use of activated initiation, which makes it possible to lower the activation energy of the radical-formation process; second, in the localization of the initiation process in the adsorption layers of the droplets, provided that it is of low efficiency in other parts of the polymerization system. This would lead to separation of the initiation zone from the zone of growth of the polymer chains and would reduce the probability of termination of the latter. Both of these factors could prove decisive for the development of the polymerization process in finely emulsified monomer droplets, bypassing the solubilization stage. The low degree of dispersity of the resulting systems would simplify isolation of the polymerizate.

We studied the activating action of N-alkylpyridinium bromides and of their pyridine-ring-substituted derivatives (the hydrocarbon radical varied from C_{15} to C_{18}) on the decomposition of cumene hydroperoxide, and the possibility of using these systems in emulsion polymerization. The kinetic regularities of the decomposition of isopropylbenzene hydroperoxide in aqueous solutions of the indicated emulsifiers and the polymerization experiments were investigated by the methods described previously ([4],[5]).

Figure 1: Kinetics of decomposition of cumene hydroperoxide in aqueous solutions of bromide N-octadecylpyridinium at various pH values of the medium.

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Since the activating action of amines on the decomposition of peroxide compounds should apparently be associated with the presence at nitrogen of a free electron pair, we studied especially thoroughly the dependence of decomposition on the pH of the medium, because with an increase in the basicity of the system, in compounds of N-alkylpyridinium bromides and their substituted derivatives, one may expect the formation of a free electron pair owing to their conversion into pyridine bases and then into pseudobases.

Figure 1 presents the decomposition of isopropylbenzene hydroperoxide in an aqueous solution of N-octadecylpyridinium bromide at a temperature of 100° at various values of the hydrogen-ion concentration (initial hydroperoxide concentration 0.04 mole/l, and emulsifier 0.01 mole/l). As follows from the data presented, the rate of hydroperoxide decomposition increases substantially with increasing pH of the medium. The time for its complete decomposition decreases to several minutes at pH 12. A similar dependence of the decomposition rate was also observed for substituted N-alkylpyridinium bromides in the pyridine ring (in the β-position

$$-\mathrm{CH}_3,\ -\mathrm{NH}_2-,\ -\mathrm{C}(=\mathrm{O})\mathrm{NH}_2.$$

Of the emulsifiers studied, the strongest activating effect is exhibited by bromide N-octadecylamide of nicotinic acid, which begins to show an activating effect already at pH 6. Thus, by changing the pH of the medium one can control the activation reaction, which makes it possible to study the polymerization process in emulsion under conditions of a gradual increase in the activating action of the adsorption layers of monomer droplets.

Fig. 1. Kinetics of decomposition of cumene hydroperoxide in aqueous solutions of bromide N-octadecylpyridinium at various pH values of the medium. *1* —without emulsifier, *2* —pH 6, *3* —pH 7, *4* —pH 8, *5* —pH 9, *6* —pH 10, *7* —pH 11, *8* —pH 12

Fig. 2. Kinetics of polymerization of styrene in an emulsion stabilized with bromide N-octadecylamide of nicotinic acid at 60°C at various pH values of the medium. *1* —pH 5, *2* —pH 6, *3* —pH 7, *4* —pH 8, *5* —pH 9

The study of the polymerization process of styrene and methyl methacrylate in aqueous emulsions stabilized with emulsifiers of the indicated class at various

Figure 2: Kinetics of polymerization of styrene in an emulsion stabilized with bromide N-octadecylamide of nicotinic acid at 60°C at various pH values of the medium.

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Fig. 3. Particle-radius distribution curve for the polymer suspension

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concentrations of hydrogen ions, and consequently at different activating effects of these ions on the decomposition of cumene hydroperoxide, showed that an increase in the activating action of the emulsifier affects the rate of polymerization as well as the dispersity of the systems formed. The kinetic curves for the yield of polystyrene when the emulsion is stabilized with bromide N-octadecylamide of nicotinic acid ($C_{\text{em}} = C_{\text{in}} = 0.01$ mol/l, $f = 1 : 9$) at various pH values of the medium are shown in Fig. 2.

A notable feature is the significant increase in the rate of the polymerization process with increasing basicity of the medium, which is in complete agreement with the data on decomposition.

The decrease in the yield of polystyrene at pH 8 and 9 may be associated with the inhibiting action of the products of interaction of the emulsifier with cumene hydroperoxide under strong activation (the system turns dark yellow), as well as with the possibility of depletion of radicals at the early stages of the development of the process.

A very remarkable fact was the sharp change in the dispersity of the polymer upon transition from nonactivated initiation (pH 5) to activated surface initiation (pH 7). In the first case the dispersity, determined by the light-scattering method, varied within the range 40–60 mμ. In the second case, a self-sedimenting, readily filterable polymer suspension was formed, with separation of a transparent aqueous phase. Figure 3 gives the particle-size distribution curve of the polymer suspension obtained in this way.

Fig. 3. Particle-radius distribution curve for the polymer suspension

Dispersion analysis was carried out by the method of Figurovskii. As is seen from the data presented, the polymer suspension is characterized by a narrow size distribution with the most probable radius of 14 μ, which corresponds to the initial droplet dispersion of the monomer. The data obtained made it possible to put forward certain assumptions concerning the topochemical features of the course of the polymerization process under conditions of surface-activated initiation.

By the beginning of polymerization practically all the monomer will be present in finely emulsified droplets of radius 10^{-4} cm, stabilized by emulsifier molecules. Under these conditions the role of the adsorption layers of the droplet increases, since it is precisely they, consisting of emulsifier molecules, that from the beginning of the process will generate free radicals into the polymerization system. Thus, active centers will arise not throughout the entire volume of the droplet, but only in a certain zone. The free radicals formed can develop into the interior of the droplet, where active centers are practically absent. As a result, the rate of termination of polymer chains will be considerably reduced, and this entails an increased molecular weight (of the same order as in latex polymerization) and high rates of the process.

Thus, it proved possible, in the case of droplet polymerization, to separate the initiation zone from the chain-growth zone. By changing the polymerization conditions associated with the initiation conditions, one can obtain either a latex or a self-sedimenting polymer suspension. Thus, for nicotinic acid *N*-octadecylamide bromide at pH 5 no interaction between the emulsifier and the initiator is observed (the hydroperoxide decomposition reaction is described by a first-order equation), i.e., surface-activated initiation is in fact absent; ordinary emulsion polymerization proceeds at a moderate rate, with formation of an ordinary stable latex. The process passes through a stage of solubilization of the monomer in the emulsifier micelles. When the pH value is raised to 7, the activating action of the emulsifier, localized in the surface layers of the monomer, becomes apparent. The polymerization process is transferred into the monomer droplets.

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