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Abstract

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ON A NEW TYPE OF POLYMER DISPERSIONS

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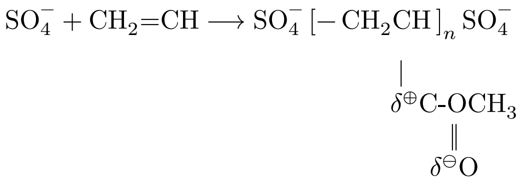
At present two methods of heterophase polymerization of monomers in an aqueous phase are known—emulsion and suspension, or granular, polymerization (^{1}). In the first case the process is carried out with the use of surface-active substances, in whose micelles, or, in the case of water-soluble monomers, in aqueous solution (^{1},^{2}), initiation and growth of polymer chains take place. As a result, latexes are formed—systems with colloidal dispersity ($d < 10^{-4}$ mm), in which the particles are protected by an adsorption layer of the surface-active substance. In the second case, polyelectrolytes are used in polymerization (^{3},^{4}), protecting the particles from premature flocculation and washed out during isolation of the polymer from the resulting coarsely dispersed suspensions ($d \gg 10^{-1}$ mm).

Experiments have also been carried out on emulsifier-free polymerization of monomers, in particular acrylates, in an aqueous phase (^{1},^{5}). In this case, however, poorly stable, low-concentration systems with coarse particle dispersity were obtained.

Here we describe the preparation of a concentrated, stable dispersion during the polymerization of methyl acrylate in an aqueous phase in the absence of an emulsifier.

It was assumed that stabilization of the particles could be achieved through polar groups at the ends of the polymer chain, formed upon initiation by salts of persulfuric acids, which upon decomposition give the ion-radicals SO_4^- (^{6},^{7}).



$$SO_4^- + CH_2{=}CH \longrightarrow SO_4^-\,[-CH_2\underset{\substack{|\\ \delta^{\oplus}C\text{-}OCH_3\\ \|\\ \delta^{\ominus}O}}{CH}]_n\,SO_4^-$$

The side ester groups of the polymer chain have a weak polarity due to the presence in them of a carbonyl.

The presence of a sulfate group at the end of the chain can lead, at a sufficiently low degree of polymerization, to the formation of a polar polymer capable of ensuring latex stability in the absence of a surface-active substance. The formation of surface-active oligomers during the polymerization of styrene initiated by potassium persulfate is indicated in work ([8]).

To obtain a stable latex on the basis of this principle, we carried out the following experiments. It was assumed that sufficient stability of the initial monomer emulsion in the absence of an emulsifier could be achieved by intensive mechanical treatment of the emulsion. Highly dispersed emulsions of methyl acrylate without emulsifier were obtained by dispersing them in a cavitator at 8000 revolutions per minute. These emulsions were then polymerized using as initiator the redox system $(NH_4)_2S_2O_8 + Na_2S_2O_4$: in one case in the presence of a molecular-weight regulator (hydroquinone), and in the other case without it.

Fig. 1. Particle shape and coagulation structures of an emulsifier-free polymethyl acrylate dispersion. Electron micrograph. *a*—particle shape, *b*—chain structures, *c*—fibrillar structures, *d*—aggregates of fibrillar structures

Fig. 2. Electron micrograph of a dispersion of high-molecular-weight polymethyl acrylate synthesized without emulsifier (*a*) and with emulsifier (*b*)

As a result, dispersions of 27% concentration were obtained, differing in their stability. Although in both cases the polymerization process was not accompanied by the formation of coagulum, nevertheless, in regulated polymerization ($\overline{P} = 700$) the dispersion retained its stability for a very long time (more than a year), whereas in polymerization in the absence of regulator ($\overline{P} = 10\,500$) a dispersion was formed that stratified one day after preparation.

Electron-microscopic study showed that, in the case of regulated polymerization, at low molecular weight of the polymer, a dispersion was formed with particles about 2100 Å in diameter, each of which, as calculation shows, contains on average about 40,000 polymer molecules. As is seen from the electron micrographs, the particles of the latex obtained have a very distinctive shape (Fig. 1a): perpendicular to the surface of the globular particle there are projections tapering in the direction of the aqueous phase, owing to the polar ends of which, evidently, stabilization of the particles is achieved.

The shape of the particles shows that in this case polymerization did not occur in micelles of the surface-active oligomer, whose formation is possible under the experimental conditions. Aggregates of polymer radicals and molecules are stabilized by their own polar groups.

When particles come into contact with one another, initially through the projections, as a result of thickening of the polymer upon extension (orientation) of small polymer chains present in the individual particles in globular form, bridges are formed between particles. Orientation leads to a decrease in the transverse dimensions of the particles and to the formation first of chainlike (Fig. 1b), and then of fibrillar structures (Fig. 1c). In the structures formed, the molecules are extended in the direction of approach of the polar groups, in connection with which their number on the interface decreases. This leads to aggregation of the fibrillar structures (Fig. 1e). Stabilization of such structures may be due to the presence of weakly polar side groups, which accounts for the existence in the dispersion of these structures alongside individual particles. The viscosity of the dispersion is 8 centipoise and does not differ from the viscosity of an ordinary latex of the same concentration. Apparently, upon increasing the concentration of the dispersion, such a structure becomes predominant and leads to its coagulation. Thus, when a dispersion with a concentration of 35% is obtained, coagulum separates in the form of a gel.

The phenomena described were found only in the case of a dispersion of a relatively low-molecular-weight polymer: a dispersion of polymer with high molecular weight, obtained under analogous conditions, has a larger particle diameter (2700 Å), which differ from the particles of the "emulsifier" methacrylate latex obtained under the same conditions by directed (chainlike) aggregation and by a somewhat smaller size (Fig. 2). Data on the particle sizes (r, V, S), degree of polymerization ($\overline{P}$), molecular weight (M), number of molecules in the particle (n), and saturation of the particle surface with sulfo groups ($S/2n$) for all the dispersions obtained are given in Table 1.

Table 1

Dispersion characteristic	$\overline{P} \cdot 10^{-3}$	$M \cdot 10^{-5}$	$r \cdot 10^{5}$, cm	$V \cdot 10^{15}$, cm^3	$S \cdot 10^{10}$, cm^2	$n \cdot 10^{-3}$	$\frac{S}{2n}$, Å^2
Without emulsifier (with regulator)	0.7	0.6	1.05	4.0	13.0	40	17.3
Without emulsifier (without regulator)	10.5	9.0	1.35	9.8	23.0	6.5	1770

Dispersion characteristic	$\overline{P} \cdot 10^{-3}$	$M \cdot 10^{-5}$	$r \cdot 10^{5}$, cm	$V \cdot 10^{15}$, cm^3	$S \cdot 10^{10}$, cm^2	$n \cdot 10^{-3}$	$\frac{S}{2n}$, Å^2
With emulsifier (without regulator)	9.5	7.0	1.62	16.0	32.2	13.7	1170

As can be seen from Table 1, the colloidal stability of dispersions obtained in the absence of an emulsifier is due to the saturation of the particle surface with sulfo groups. At a lower molecular weight of the polymer, the relative content of these groups is greater, which ensures the stability of the dispersion; at a high molecular weight, the quantity of sulfo groups contained in the polymer is insufficient for stable stabilization of the dispersion, and therefore the introduction of a surfactant into it is required.

The polarity of the polymer obtained as a result of polymerization initiated by persulfate apparently explains the anomaly, found by one of the authors, in the adsorption of an ionic emulsifier during the emulsion polymerization of methyl methacrylate ([9]). The cause of this anomaly is probably the presence of polar groups on the surface of the latex particles, which hinder the formation on it of an oriented adsorption layer of emulsifier.

As a result of the work, a new type of polymer dispersion has been obtained, in which the stability and the form of dispersion of the polymer are determined by its polarity. Electron-microscopic investigation showed the distinctive character of the particle shape and made it possible to trace the emergence of precoagulation structures in this type of dispersion: particles of a colloidal degree of dispersion aggregate through polar groups, first forming chain structures, which, owing to the orientation of the macromolecules, pass into fibrillar structures that fold into bundles.

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