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## The Emulsion Polymerization of Styrene in the Presence of Nonionic Emulsifiers

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### ABSTRACT

The emulsion polymerization of styrene was investigated in the presence of nonionic emulsifiers with different degrees of ethylene epoxydization and their mixtures with ionic emulsifiers. In the presence of nonionic emulsifiers the polymerization processes are shown to differ essentially from the analogous processes in the presence of ionic surface-active substances. The characteristic features of such systems are invariability of latex particle average size from the degree of conversion 8-10% and high extent of adsorptive layer saturation in the course of the whole process.

The influence of emulsifier and initiator concentration and of the volume ratio of monomer to emulsifier solution on the polymerization rate, polymer average molecular weight, and latex particle average size were studied.

The polymerization of styrene in the presence of binary mixtures of ionic and nonionic emulsifiers was studied. The polymerization rate, polymer molecular weights, and latex particle sizes are shown not to change additively with a change of the mixed emulsifier components ratio. The data obtained are evaluated quantitatively.

## INTRODUCTION

The considerable interest shown lately in the nonionic surface-active substances (SAS) is related to the fact that they have the features of traditional anion- and cation-active emulsifiers (the capability for micelle formation, colloidal solubilization of hydrocarbons, etc.) and at the same time are characterized by the presence of the specific hydrophilic part of the molecule.

The important advantage of the nonionic ethylene-epoxidized SAS is the possibility of easily adjusting their hydrophilic properties by changing the quantity of added ethylene epoxide (EE); this permits products with optimum properties for various fields of application to be obtained.

Work devoted to the investigation of the aggregative stability of latexes prepared with nonionic SAS has revealed the high stability of such systems.

The polymers formed are characterized by the absence of electrolyte impurities, and this can be of interest for their commercial application.

A relatively small number of publications [1-6] is devoted to the investigation of emulsion polymerization with nonionic emulsifiers. The systematic study of the kinetics and mechanism of emulsion polymerization in the presence of nonionic emulsifiers, which was undertaken by S. S. Medvedev and his collaborators, has revealed some important features of this type of polymerization [7-13]. We have studied the emulsion polymerization of styrene in the presence of nonionic emulsifiers of several types: ethylene-epoxidized alcohols, alkyl phenols, and polypropylene glycols. Benzoyl peroxide (BP) and azobisisobutyronitrile (AIBN) were used as initiators.

## EXPERIMENTAL

AIBN, BP, and styrene were purified according to the usual methods. The styrene fraction used had a boiling point of  $41^{\circ}\text{C}$  (16 Torr,  $d_4^{20} = 0.9060$ ,  $n_D^{20} = 1.5450$ ).

Emulsifiers C-8, C-20, C-30, and C-40 were synthesized from cetyl alcohol and ethylene epoxide at  $130^{\circ}\text{C}$ ; the catalyst was NaOH (0.1 wt% of cetyl alcohol). The emulsifiers were white, hard products which contained 8 to 40 ethylene epoxide units per molecule, respectively. The properties of the other emulsifiers used in this work are shown in Table 1.

TABLE 1. Properties of Nonionic Emulsifiers

Emulsifier	Raw material	Number of ethylene epoxide units	Molecular weight
OC-20A	Narrow fraction of fatty alcohols (mainly octadecyl alcohol)	20	1,152
OC-20B	Fatty alcohols mixture of the average composition $C_{17}H_{35}OH$	20	1,136
P-228	Polypropylene glycol	200	11,000
P-68	Polypropylene glycol	150	8,200
T-707	Ethylenediamine polypropylene glycol	175	11,000

The following substances were used as ionic emulsifiers: emulsifier MK, the sodium alkylsulfonates mixture of average composition  $C_{15}H_{31}SO_3Na$  (used with purification); and cetylpyridinium chloride (CPC), the commercial product was recrystallized twice from acetone and dried in vacuum. Benzene, toluene, and methanol, products of the "pure for analysis" grade were dried over calcium chloride or copper sulfate and distilled. Twice distilled water was used for the water phase. The second distillation was carried out with an alkaline solution of potassium permanganate. The pH value of the water was controlled.

The kinetic studies were carried out by the vacuum dilatometric method. The molecular weights of the polymers were measured by means of light scattering and viscometric methods. Latex particle sizes were measured by means of the electron microscope and nephelometer.

## RESULTS AND DISCUSSION

One of the main question in the theory of emulsion polymerization is that of the topochemistry of polymerization process. The possible locations where elementary reactions may occur are monomeric

droplets, the monomer-water interface, emulsifier micelles saturated with monomer, and the water solution of monomer. One location may be predominant, depending on the nature of emulsifier, monomer, and initiator.

It has been shown that polymerization of monomers nonsoluble in water begins in micelles containing colloiddally dissolved monomer, the characteristic features of these systems being the prolonged coexistence of emulsion droplets and polymer-monomeric particles, and the continuous increase of latex particle sizes up to the depletion of droplets.

In the case of systems with nonionic emulsifiers of the types mentioned above, the measurement of the latex particle average sizes, depending on the degree of conversion, shows that in a wide range of SAS concentrations the latex particle sizes remain constant (Fig. 1) from practically the beginning up to the end of the process (the measurements were carried out with a degree of conversion equal to 8-10%).

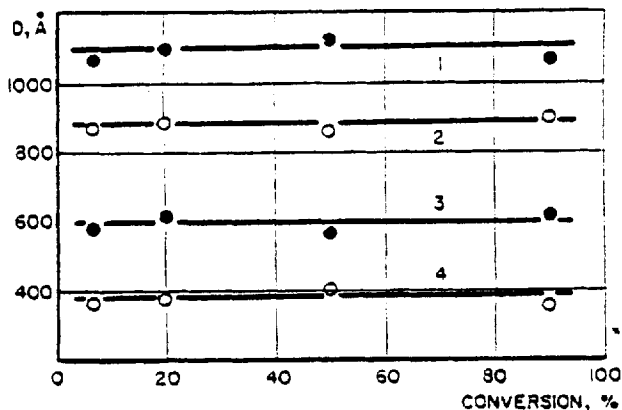


FIG. 1. The change of polystyrene latex particles sizes with conversion. Initiator AIBN ( $1.0 \times 10^{-4}$  mole/ml monomer). Emulsifier (mole/ml monomer  $\times 10^4$ ): 1, C-20 (1.97); 2, C-30 (1.60); 3, C-40 (1.90); and 4, OC-20A (3.50). Temperature: 50°C.

In this respect it is interesting to note some results of Orr and Breitman's work concerning the study of the areas occupied by the molecules of surface-active substances of different natures on the surface of polymer-monomer particles [17, 18]. It is highly

important that in contrast to ionic emulsion systems, the authors mentioned could not synthesize latexes stabilized only with nonionic surface-active substances when their concentrations in the water phase were less than the critical concentration of micelle formation.

Hence for the nonionic emulsifiers the complete saturation and invariability of sizes of latex particles is predetermined by the mechanism of latex particle formation itself.

Calculations show that from the beginning of polymerization the quantity of monomer in any particle is enough for the formation of several dozen polymer chains with a degree of polymerization equal to  $10^4 - 10^5$ .

The peculiarity of the system investigated is revealed in experiments with the addition of Emulsifier C-40 in the course of styrene polymerization (5, 15, 30, 40, and 50% conversion) (Fig. 2).

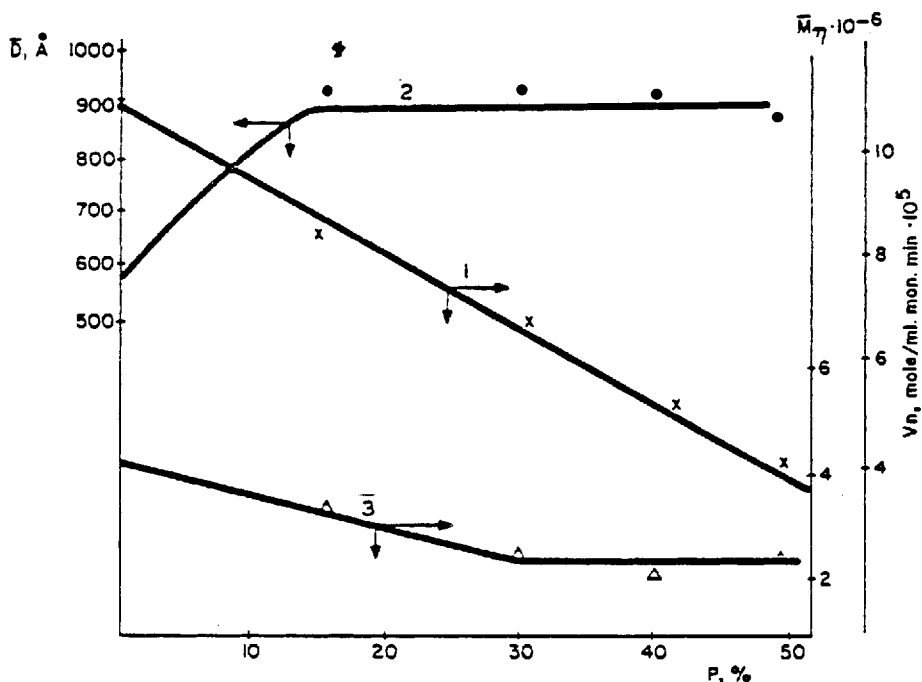


FIG. 2. Dependence of polymerization rate (1), latex particle sizes (2), and molecular weight of polymers (3) on the degree of conversion at which the addition of C-40 was made.

It is known that the addition of emulsifier in the course of polymerization with ionic emulsifiers [15] causes an increase of the polymerization rate, and this is usually explained by the increase of the adsorptive layers total surface [16]. The rate increase takes place up to the point at which the saturation of surface layers is achieved. Prior to this point the more emulsifier added, the more the rate increases. The addition of nonionic Emulsifier C-40 also causes an increase of the polymerization rate and the polymer molecular weights. The greater the degree of conversion at which the additional emulsifier is introduced; the smaller is the increase of rate and molecular weight (Fig. 2). Latexes obtained after introducing additional emulsifier have bimodal distribution, each set of particles being monodisperse (Figs. 2a and 3). One of the particle sets is in the size region of the initial latex particles, and the second one corresponds to a new ratio of emulsifier/monomer in the system.

Taking into consideration the invariability of latex particle sizes in the course of polymerization and the complete saturation of their surface layers with emulsifiers, one can conclude that polymerization takes place in the discrete latex particles forming due to the mass transfer of nonionic emulsifier at the water/macrodroplet interface [6, 13]. The presence of a firm interphase layer on the surface of macrodroplets prevents the diffusion of monomer from one droplet to the others and to the discrete particles where polymerization occurs. The monomer from macrodroplets is spent for the formation of new particles, the number of which increases in the course of polymerization up to the depletion of monomer in macrodroplets.

The introduction of an additional quantity of emulsifier causes the redistribution of emulsifier in the system, the more intensive mass-exchange and the formation of new latex particles with a size corresponding to new emulsifier/monomer ratio.

The influence of the length of the hydrophilic part of the nonionic emulsifier molecule on the main relationships of the process was studied with a number of surface-active substances synthesized for this purpose (Emulsifiers C-8, C-20, C-30, and C-40).

In all the experiments in which the polymerization rate was determined, the polymer yield was proportional to time and depended little on the monomer concentration (changing in the course of polymerization) up to relatively high conversion degrees of the order 40-50% (Fig. 4).

Comparison of the data for the emulsion polymerization of styrene with stabilizers having various degrees of ethylene epoxidization showed that the main relationships of the polymerization process depend substantially on the length of the hydrophilic part of the SAS molecule.

In the presence of SAS with a ethylene epoxidization degree equal to 8, the polymerization rate is close to that of bulk polymerization

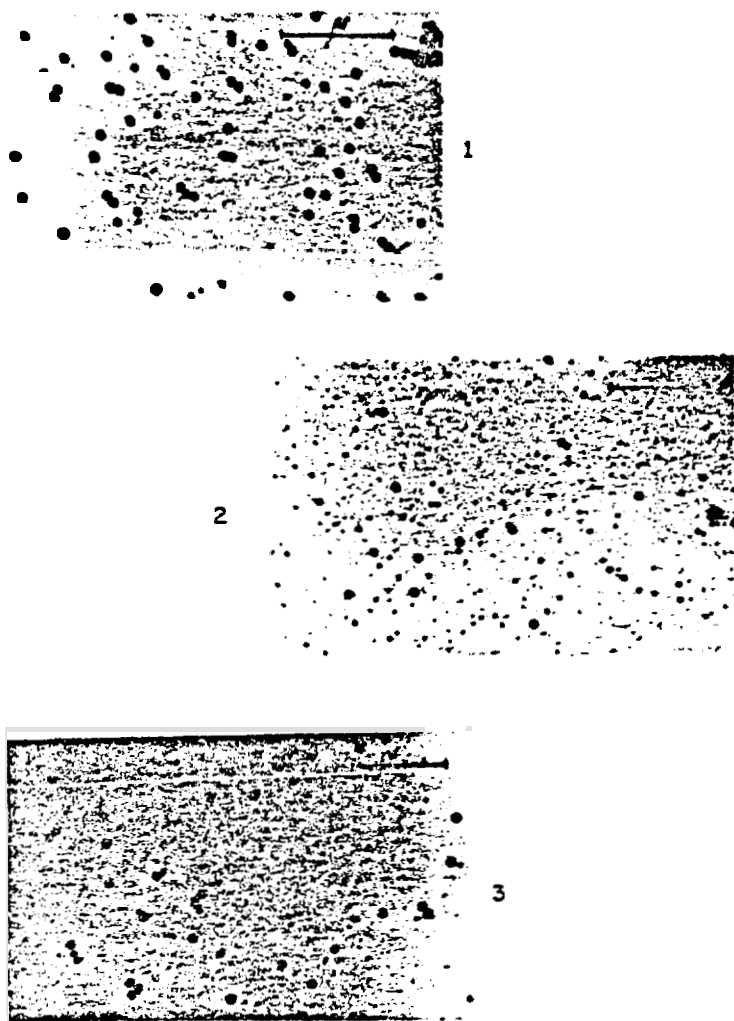


FIG. 2a. Microphotographs of latexes obtained after the addition of C-40 at 15% (2) and 40% (3) degree of conversion. There was no addition for Microphotograph 1.

(Curves 4 and 5 in Fig. 4); the suspension formed has particles with diameters of the order of  $10^4$  Å, and the average molecular weight of the polymer is about  $5 \times 10^4$ .

With a certain degree of ethylene epoxydization (in this case 20



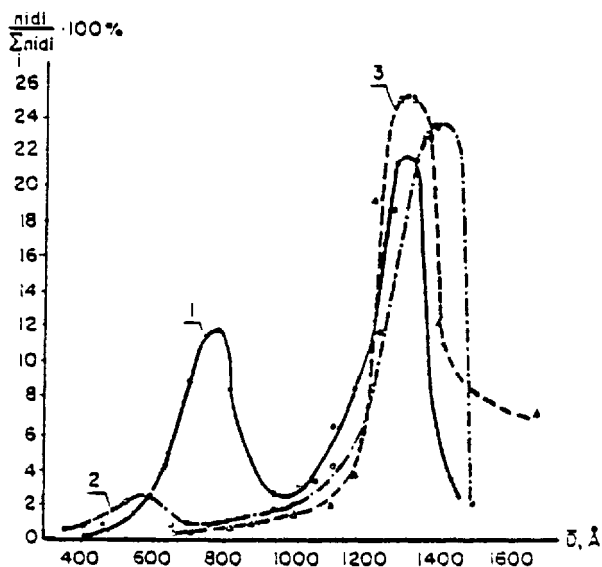


FIG. 3. Particle sizes distribution of latexes obtained after the addition of C-40 at 15% (1) and 40% (2) degree of conversion and without the addition of C-40 (3).

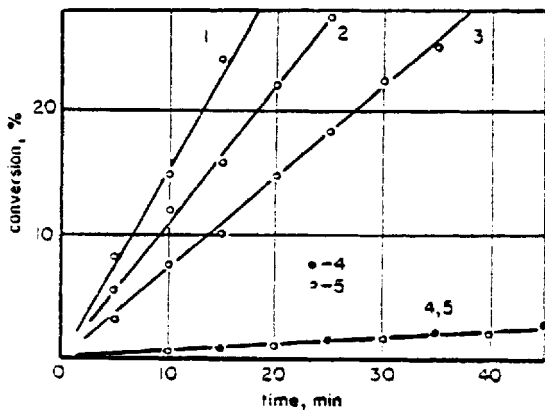


FIG. 4. Polymer yield-time dependence. Emulsifier: (1) C-40; (2) C-30; (3) C-20; (4) C-8; (5) bulk polymerization of styrene. Emulsifier concentration:  $2.9 \times 10^{-4}$  mole/ml monomer. Initiator: AIBN ( $1.0 \times 10^{-4}$  mole/ml monomer). Temperature:  $50^\circ$ .

ethylene epoxide groups per SAS molecule), the high rates typical for emulsion polymerization are achieved, and latexes with a high degree of dispersity (latex particles diameter 400-2000 Å) and high molecular weight polymers are formed.

A further increase in the length of the hydrophilic part of the SAS molecule results in raising the efficiency of SAS as an emulsifier. At a constant molar emulsifier concentration, the greater the degree of ethylene epoxydization the greater is the number of particles formed (of smaller size) and the higher are the polymerization rate and polymer molecular weight (Fig. 4, Table 2).

TABLE 2. The Influence of the Ethylene Epoxydization Degree of Cetyl Alcohol on the Styrene Polymerization Rate ( $R_p$ ), Latex Particle Average Diameter ( $\bar{D}$ ), and Polymer Average Molecular Weight ( $\bar{M}$ )<sup>a</sup>

Number of EE groups per SAS molecule	$R_p \times 10^4$ mole/ml monomer min	$\bar{M}_\eta \times 10^{-6}$	$\bar{D}$ (Å) <sup>b</sup>
8	0.11	0.05	10,000
20	0.75	2.66	1,120
30	1.21	3.90	780
40	1.51	4.70	610

<sup>a</sup>Emulsifier concentration,  $2.0 \times 10^{-4}$  mole/ml monomer; AIBN concentration,  $1 \times 10^{-4}$  mole/ml monomer; volume ratio oil/water, 1:2; temperature, 50°.

<sup>b</sup>Polymer molecular weight and latex particle average diameters were measured at 30% conversion.

The influence of the length of the polar part in the nonionic emulsifier molecule on polymerization is probably related to the increase of the interface area stabilized by one SAS molecule. This is proved by experiments in which the latexes obtained by means of ionic emulsifiers were titrated with nonionic emulsifiers.

In the range of ethylene epoxydization investigated, the degree the surface area occupied by one emulsifier molecule in an adsorptive layer on the polymer-monomer particle surface is proportional to the length of hydrophilic part of the SAS molecule (Fig. 5).

For the emulsifiers with various degrees of ethylene epoxydization mentioned above, the decomposition of benzoyl peroxide was studied in a water-toluene emulsion. The results of these experiments, presented in Fig. 6, show that the decomposition of peroxide is

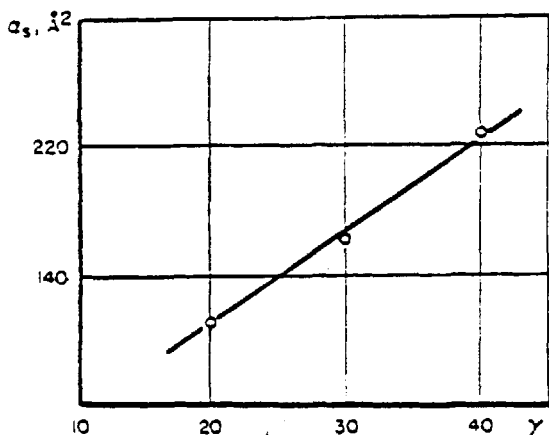


FIG. 5. The dependence of the area occupied by a molecule of nonionic emulsifier on the interface ( $\alpha_s$ ) on the degree of emulsifier ethylene epoxydization ( $\gamma$ ). Emulsifiers: C-20, C-30, and C-40.

accelerated with the increase of the length of hydrophilic part of the emulsifier molecule.

The comparison of the results represented in Figs. 4-6, that is, the dependence of polymerization and initiator decomposition rates on the surface area occupied by emulsifier molecules with various degree of ethylene epoxydization, allows the conclusion that the initiator decomposition occurs near the boundary dividing the polar and nonpolar phases on the surface of latex particles.

This fact is of primary importance because it points out the hydrophilic groups in an emulsifier molecule as a factor favoring initiator decomposition and effective initiation reactions.

The possibility of mass exchange, which is supposed to occur with ionic emulsifiers, is completely absent in this case. Each particle may be considered as an independent microsystem in which initiation occurs on the particle surface but where propagation and termination of polymer chains occur in particle volume. In this case the ratio between particle surface and volume will be the parameter determining the polymerization process relationships in nonionic emulsion systems. The experimental results and their consideration, given below, support this assumption. The quantities of all initial and intermediate compounds in what follows are related to the volume unit of monomer (ml).

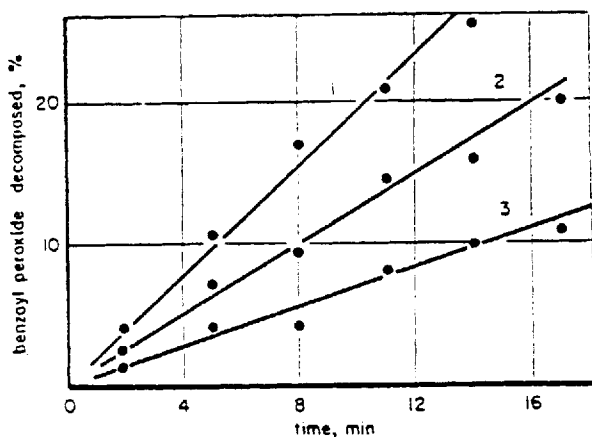


FIG. 6. BP decomposition vs time in water-toluene emulsion stabilized with emulsifiers: (1) C-40; (2) C-30; (3) C-20. Emulsifier concentration: 0.05 mole/liter water. BP initial concentration: 0.05 mole/liter toluene. Phase ratio toluene/water = 1:3 (vol). Temperature: 60°.

In the general case the initiator distribution between particle surface area and volume can be expressed by

$$\frac{\alpha [I]}{1 + b [I]} = K_s [I]_s \quad (1)$$

where  $[I]$  is the initiator concentration,  $[I]_s$  is the concentration of initiator on the particle surface occupied by emulsifier molecules, and  $K_s$  is the constant of proportionality.

The surface  $S$  of the particles completely covered with an emulsifier layer is connected with the emulsifier quantity  $E$  by

$$S = \alpha_s E N_A \quad (2)$$

or, if it is attributed to the volume of the organic phase (ml)

$$S/V = \alpha_s E / V N_A \quad (3)$$

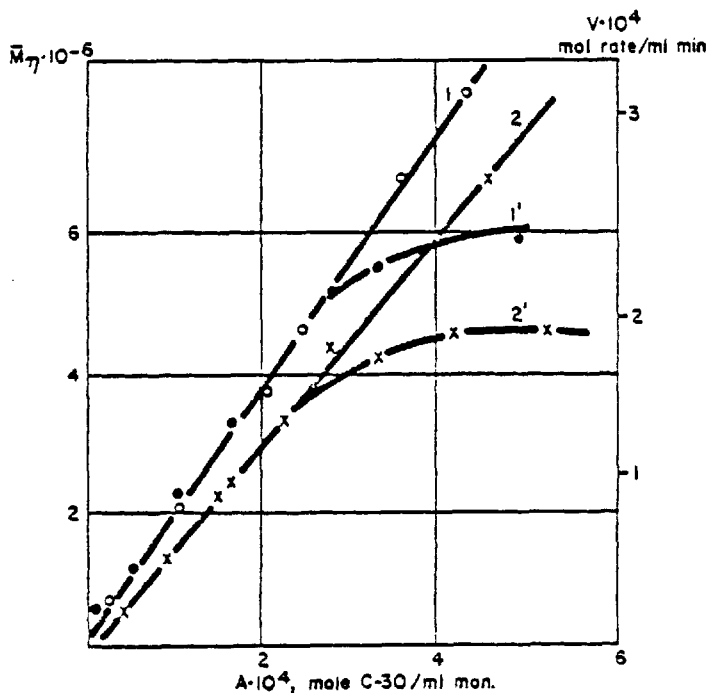


FIG. 7. The dependence of polymerization rate ( $R_p$ ) (a) and polystyrene average molecular weights ( $\bar{M}$ ) (b) on the ratio emulsifier/monomer. Emulsifier: C-30. Curves 1 and 2: the phase ratio changed at constant emulsifier concentration in water phase. Curves 1' and 2': emulsifier concentration changed at constant phase ratio. Initiator: AIBN ( $1.0 \times 10^{-4}$  mole/ml monomer). Temperature:  $50^\circ$ .

where  $\alpha_s$  is the area occupied by one emulsifier molecule on the surface of latex particles and  $N_A$  is Avogadro's number.

It is necessary to emphasize that, as it follows from the experimental results obtained in this work, the rate and average degree of polymerization are proportional to the value  $E/V$  in a broad range of emulsifier/monomer ratios (Fig. 7).

The following relationships are true for the stationary state of a polymerization system

$$\beta K_d [I]_s = 2 K_t [P']^2 \quad (4)$$

$$[P^*] = \left( \beta \frac{K_d}{2 K_t} \right)^{\frac{1}{2}} ([I]_s)^{\frac{1}{2}} \quad (5)$$

where  $\beta$  is the initiation efficiency, and  $K_d$  and  $K_t$  are the rate constants of initiator decomposition and propagating chains termination, respectively.

Taking into account relationships (3) and (5), the expression for the total rate of polymerization in the presence of the ethylene-epoxidized surface-active substances used can be represented by

$$R_p = K_d \left( \beta \frac{K_d}{2 K_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} N_A \delta \gamma E / V [M] \quad (6)$$

where  $\delta \gamma = \alpha_s$  (Fig. 5),  $\delta$  is the part of the surface per one EP group in an adsorptive layer, and  $\gamma$  is the number of EP groups in an emulsifier molecule.

The average degree of polymerization is determined by the analogous expression

$$\overline{DP} = \frac{K_p}{K_t^{\frac{1}{2}} (\beta K_d)^{\frac{1}{2}}} [I]^{-\frac{1}{2}} N_A^{-\frac{1}{2}} \delta \gamma E / V [M] \quad (7)$$

Equations (6) and (7) can be presented in a form suitable for experimental checking:

$$\left( \frac{\gamma E}{R_p V} \right)^2 = \frac{A_4^2}{d} \frac{1}{[I]} + \frac{A_4^2 b}{d} \quad (8)$$

$$\left( \frac{DPV}{\gamma E} \right)^2 = \frac{B_4^2}{d} \frac{1}{[I]} + \frac{B_4 b}{d} \quad (9)$$

where

$$A = K_p \left( \beta \frac{K_d}{K_t} \right)^{\frac{1}{2}} \delta N_A [M] \quad (10)$$

$$B = \frac{K_p}{K_t^{1/2}} (\beta K_d)^{-1/2} \delta N_A [M] \quad (11)$$

The dependencies of  $R_p$  and  $\bar{M}$  on the initiator concentration calculated from the Eqs. (8) and (9) correspond to experimental data (Fig. 8).

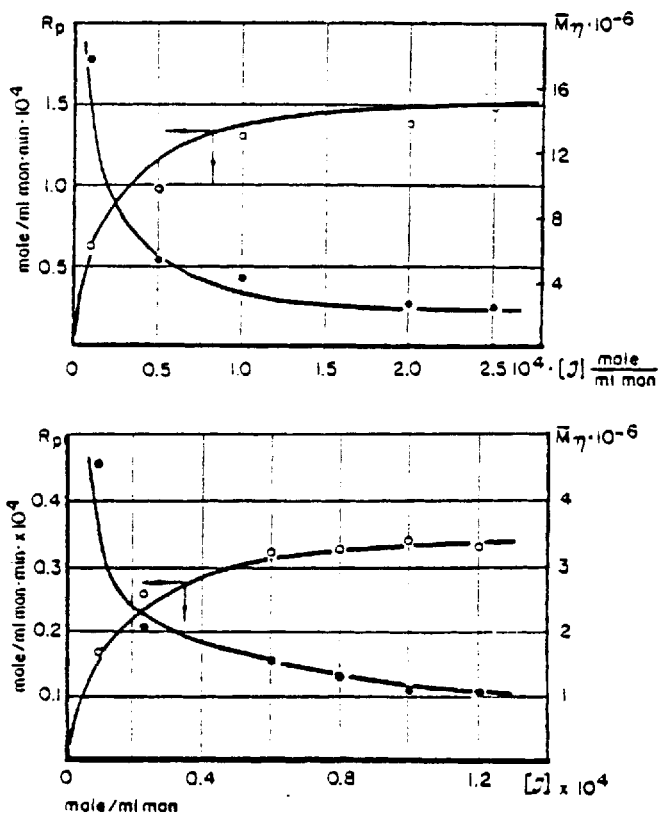


FIG. 8. The dependence of polymerization rate and polystyrene average molecular weight on the concentration of the initiator AIBN. Emulsifier: (top) C-30 ( $0.53 \times 10^{-4}$  mole/ml monomer); (bottom) C-40 ( $1.71 \times 10^{-4}$  mole/ml monomer). Temperature:  $50^\circ$ . Calculated from Eqs. (8) and (9).

It is interesting to note that the latter two relationships can be represented as expressions very close in content to the conclusions obtained in the Stockmayer-Van der Hoff approximation [19, 20]. Indeed, the parameter  $S/V$  (proportional to  $E/V$ ) is related to the degree of particle dispersity  $1/D$  by

$$S/V = 6(1/D) \quad (12)$$

which is true under the following condition.

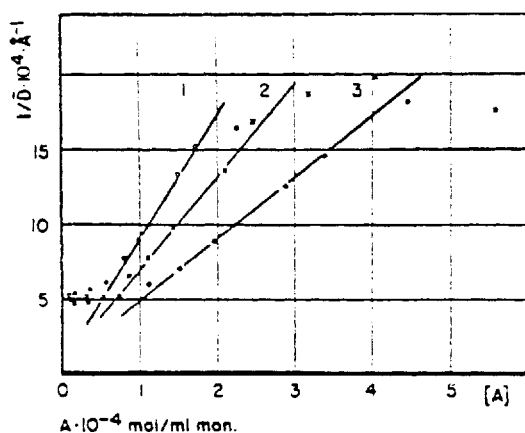


FIG. 9. The dependence of the  $1/\bar{D}$  value on the ratio of emulsifier to monomer. Emulsifier: (1) C-40; (2) C-30; (3) C-20. Initiator: AIBN ( $1.0 \times 10^{-4}$  mole/ml monomer). Temperature:  $50^\circ$ .

The entire monomer is spent only for the formation of latex particles, and the latex particle sizes remain constant in the course of polymerization.

The experimental results concerning the measurement of particle average size as a  $1/D$  function of  $E$  are represented in Fig. 9.

Relationships (6) and (7) can be represented in the following form by taking into account expression (12):

$$R_p = 6K_p/R_t^{\frac{1}{2}} (1/D)(\beta K_d)^{\frac{1}{2}} [I]_s^{\frac{1}{2}} [M] \quad (13)$$



$$\overline{DP} = 6(1/D) \frac{K_p}{K_t^{\frac{1}{2}}(\beta K_d)^{\frac{1}{2}}} [I]^{-\frac{1}{2}} [M] \quad (14)$$

These expressions for the total rate and degree of polymerization differ by  $[6 \times (1/D) = S/V]$  from the analogous dependencies for solution and bulk polymerization, this differing expression simply determining the degree of dispersity of the reaction mixture.

Thus in the case of nonionic emulsifiers there is a possibility of distinguishing the so-called "factor of dispersity" [12] in an explicit form.

Some results obtained when processes of emulsion polymerization are investigated with two-component mixtures of emulsifiers are worthy of attention.

The mixtures of ionic and nonionic emulsifiers are of particular interest because they allow the obtaining in polymerization systems of adsorptive layers that consist of molecules which differing sharply because of the nature of their hydrophilic parts.

We studied several two-component mixtures. Figure 10 shows the dependencies of polymerization rate, polymer average molecular weight, and latex particle size on the ratio between ionic and nonionic components in the mixed emulsifier.

The common characteristic feature in the relationships represented in these figures is the nonadditive change in polymerization rate and polymer average molecular weight depending on the ratio of components in the mixed emulsifier. In both cases the change in latex particles size is the result of the change in polymerization rate and polymer average molecular weight.

These data were supplemented by the results of investigating micellar molecular weight changes taking place in water solutions of mixed emulsifiers (Fig. 11 and 12).

The quantitative measurement of hydrate water bonded with emulsifier, which depends on the composition of the mixture, showed (Fig. 12) that the maximum of mixed emulsifier hydration corresponds to the maximum deviation of polymerization rate, polymer average molecular weight, and latex particle average size from additive values. As we showed earlier [14], the action of any factor which has as its consequence the changing of the micellar molecular weight in emulsifier water solutions (temperature, electrolytes, introduction of the second component, etc.) is comparable with the action of the same factor on the polymerization system.

The change in the degree of mixed emulsifier hydration accompanying the process of micellar molecular weight change in water solutions

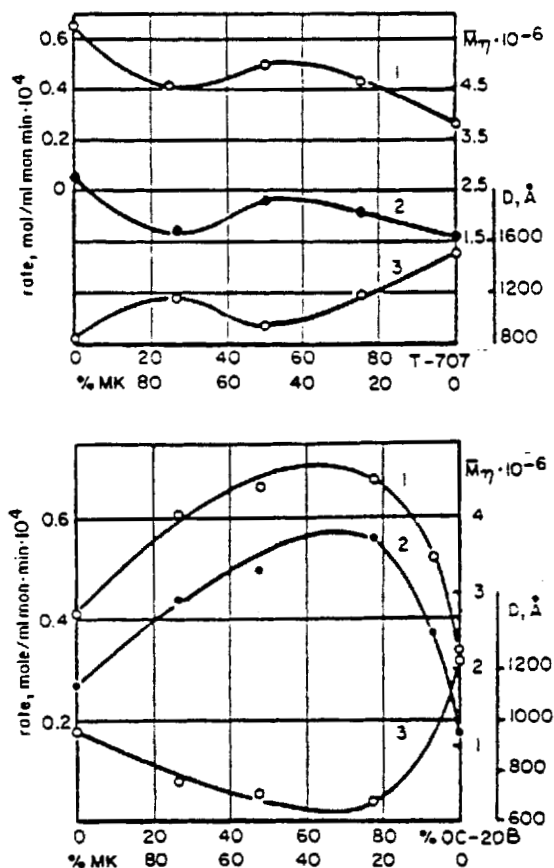


FIG. 10. The dependencies of polymerization rate (1), average molecular weight (2), and latex particle average diameters (3) on the ratio of ionic and nonionic emulsifiers in the mixture. Ionic component: Emulsifier MK: Nonionic component: (top) T-707; (bottom) OC-20B. Total concentration of emulsifiers mixture: 2.0 g/100 ml water. Initiator: AIBN (1 wt% to monomer). Temperature: 50°.

indicates the change of the surface area which can be stabilized by one conditional molecule of mixed surface-active substance in a polymerization system.

The change of active surface area will obviously cause a change in

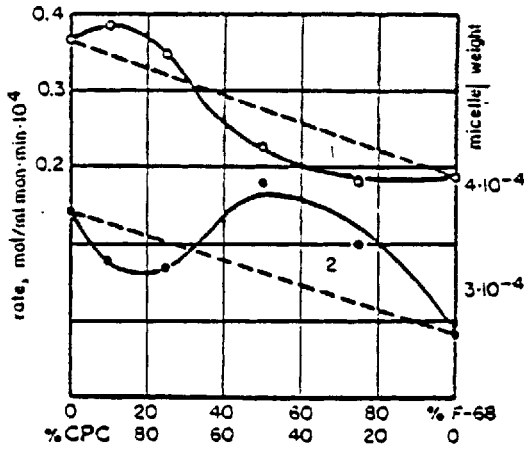


FIG. 11. The dependences of polymerization rate (1) and micellar weights (2) on the ratio of CPC to F-68 in the mixture. Total concentration of emulsifiers mixture: 2.0 g/100 ml water. Initiator: AIBN (10 wt% to monomer). Temperature: 50°.

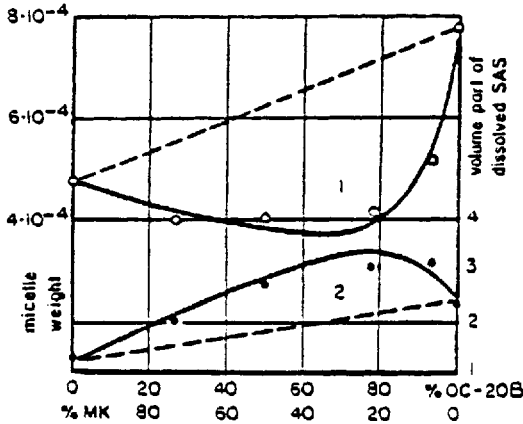


FIG. 12. The change of micellar weight (1) and the volume part of dissolved SAS (2) with the ratio of components in the MK and OC-20B mixture.

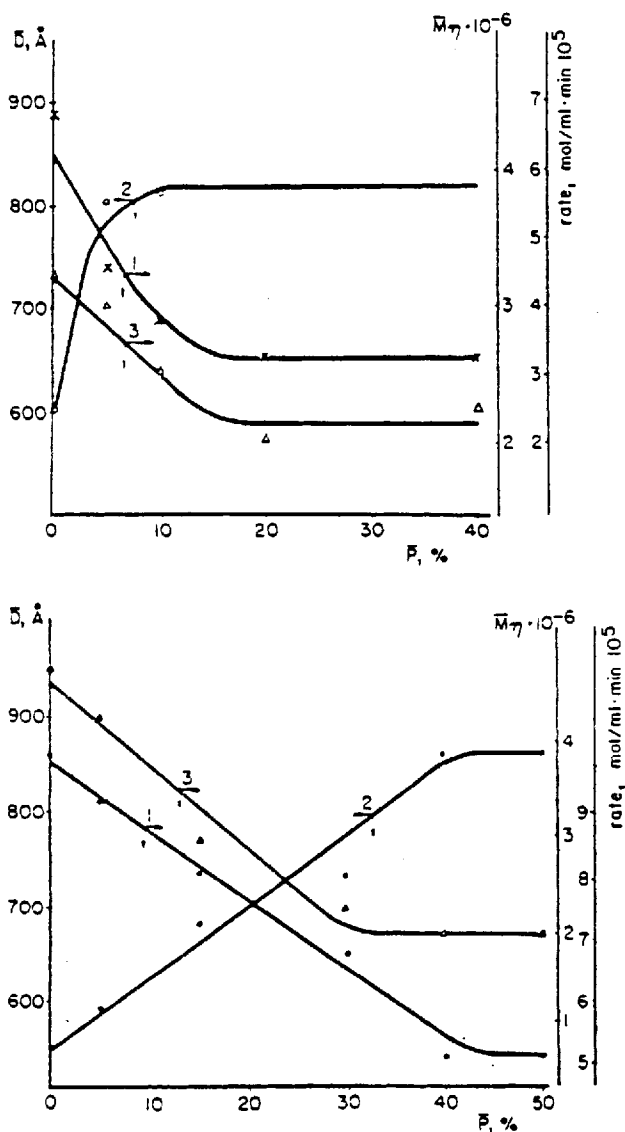


FIG. 13. Dependence of polymerization rate (1), molecular weights (2), and latex particles average diameters (3) on the degree of conversion at which the addition was made of ionic and nonionic emulsifiers in the mixture. ———— Top: CPC and C-40 mixtures, with the total concentration of the emulsifier mixture being 2 g/100 ml water, AIBN as initiator ( $1.1 \times 10^{-4}$  mole/ml monomer), and a temperature of  $50^\circ\text{C}$ . Bottom: Sodium alkylsulfonate and C-40 mixtures, with the total concentration of the emulsifier mixture being 4 g/100 ml water, AIBN as initiator ( $2.2 \times 10^{-4}$  mole/ml monomer), and a temperature of  $50^\circ\text{C}$ .

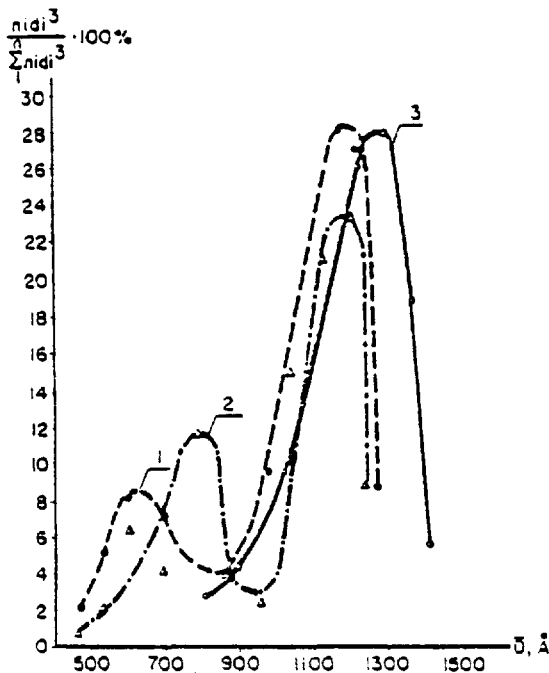


FIG. 14. Particle size distribution of latexes obtained after the addition of Na-alkylsulfonate/C-40 at 40% (1) and 15% (2) degree of conversion and without addition (3).

the degree of dispersity, and this is directly connected with the main relationships of the emulsion polymerization process.

For the elucidation of kinetic peculiarities and the topochemistry of polymerization in the presence of emulsifiers mixture, the influence of monomer conversion, the emulsifier and initiator concentrations, the additions of the emulsifying mixture in the course of the process on the polymerization rate, polymer molecular weights, and latex particle average sizes were studied. The weight ratio of ionic to nonionic emulsifier was kept equal to 40/60 and 50/50 for C-40/sodium alkylsulfonate and C-40/CPC, respectively (Fig. 13).

Latex particle average sizes remain constant in the course of polymerization. The data concerning the influence of emulsifying mixture additions are consistent with the results represented above for C-40 (Figs. 3 and 14).

The results obtained illustrate the predominant role of the non-ionic component in the polymerization process for the range of emulsifier component ratios investigated.

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