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SEMICONTINUOUS EMULSION POLYMERIZATION OF VINYL ACETATE. XI. INFLUENCE OF INITIATOR CONCENTRATION ON HOMOPOLYMERIZATION AND COPOLYMERIZATION IN THE PRESENCE OF A SULFOSUCCINATE SURFACTANT

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ABSTRACT

In the homopolymerization and copolymerization of vinyl acetate with dibutyl maleate in the presence of the sodium salt of sulfosuccinic acid semiester with nonylphenol ethoxylated with 25 mol ethylene oxide, the initiator, potassium persulfate (KPS), has a higher decomposition rate than in water even after consumption of monomer. The value of the initiator productivity, P , defined as the ratio of the formed polymer over the decomposed KPS, decreases as the batch stage of the semicontinuous process proceeds. The initiator reacts either with free surfactant molecules or with those grafted on poly(vinyl acetate) chains. During the stage of continuous addition of monomers and KPS, a smaller initiator concentration no longer provides proportionality between the added and decomposed amounts of initiator. The increased monomer concentration at the beginning of continuous addition causes the rate of KPS splitting to decrease as most of the surfactant is bound to the surface monomer/polymer particles.

INTRODUCTION

The kinetics of semicontinuous emulsion homopolymerization and copolymerization of vinyl acetate (VAc) with dibutyl maleate (DBM) was studied in a previous contribution [1]. It was shown that in the presence of the surfactant, i.e., sodium salt of the sulfosuccinic acid semiester with polyoxyethylene (25) *p*-nonylphenol (NPEO₂₅SS), the rate of polymer formation and the splitting of the initiator (potassium persulfate, KPS) decreased with an increase in the less polar monomer (DBM).

The reaction order of the polymerization and of initiator splitting, compared to the initiator, ranged from 0.1 to 0.33 and 0.7 to 0.5 for homopolymerization and copolymerization, respectively.

These results show that the initiator concentration plays a major part in the advancement of polymerization initiation and in KPS decomposition reactions. Therefore, we consider it important to show the evolution of both reactions during the batch and the continuous stage of the semicontinuous process of vinyl acetate emulsion polymerization.

EXPERIMENTAL

Materials

Vinyl acetate was purified by rectification.

Dibutyl maleate was purified by distillation under reduced pressure.

The sodium salt of the sulfosuccinic acid semiester with nonylphenol ethoxylated with 25 mol ethylene oxide was prepared in the laboratory according to the known method [2].

Highly pure potassium persulfate (LOBA-CHEMIE) was used without further purification.

Procedure

The procedure is essentially that given in References 1 and 3-5. Polymerizations were conducted in a glass autoclave equipped with anchor agitator (a stirring rate of 200 rpm). The process consists of two steps, one conducted batchwise (I) and the other continuously (II). The nature and amounts of the starting materials are presented in Table 1.

For copolymerization, a mixture of 60/40 (vol) VAc/DBM was used.

The initiator was fed into the polymerization mixture at a temperature above 65°C, then the mixture was stirred for 1 hour, and samples were collected in which the monomer and the initiator conversion were determined.

After 1 hour the temperature of the polymerization medium had reached 70°C. Addition of monomer (840 g) was started and continued for 5 hours; the same amount of initiator as was used in the batch stage (dissolved in 105 cm³ water) was simultaneously added. During this continuous monomer and initiator addition, sampling was also performed to evaluate the amount of polymer obtained and that of decomposed initiator. The data shown in the figures refer to the above-mentioned reaction conditions.

TABLE 1. Nature and Amount of the Reactants

	Batch polymerization (I)			Continuous polymerization (II), g
	g	10^2 mol	g/100 cm ³ H ₂ O	
H ₂ O	655			105
NPEO ₂ SS (E)	38; 25	2.46; 1.55	5.8; 3.7	
Monomer	100			840
KPS	0.5–2.1	0.185–0.77	0.076–0.32	0.5–2.1

The monomer conversion was determined gravimetrically. The fraction of nondecomposed initiator still present in the reaction medium was determined by cerimetry [6].

Samples of emulsions taken at different times were made into films by drying at room temperature. These films were then successively extracted, for 8 hours, in boiling water and benzene. Three fractions were thus isolated: a water-soluble, a benzene-soluble, and an insoluble fraction in both these solvents.

The intrinsic viscosity of the benzene-soluble fractions was determined in benzene at 20°C using an Ubbelohde viscometer.

RESULTS AND DISCUSSIONS

Formation of polymer and of decomposition of the initiator during the batch stage of polymerization is shown in Fig. 1.

It is noteworthy that the rate of decomposition of the initiator is still significant even when the polymerization rate is considerably reduced. The rates of polymer formation and initiator decomposition were much higher in the case of homopolymerization.

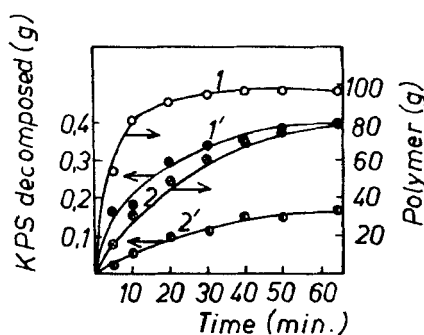


FIG. 1. Time evolution of the amounts of polymer (1, 2) and of decomposed initiator (1', 2') (1, VAc; 2, VAc/DBM = 60/40; $[KPS]_0 = 0.5$ g; $[E]_0 = 3.7$ g/100 mL H₂O).

The presence of all oxidizable groups of the reactants in the emulsion polymerization medium increases the splitting rate of the persulfate-type initiator [7]. Surfactants [7–24] and monomers [5, 7, 8, 10–13, 25–33] enhance the decomposition rate of the initiator. As the monomer concentration decreases, the emulsifier remaining in the reaction medium, a very active reaction partner for KPS, is responsible for maintaining the high decomposition rate of the initiator.

Interactions between monomers and surfactants depend on the monomer polarity. Monomer solubilization in micellar systems occurs by selective interactions between nonpolar monomers and the hydrophobic part of the micelles whereas polar monomers interact with the hydrophilic part of the latter [37–41].

Interactions between the surfactant and the monomer droplets, occurring at the beginning of the polymerization, are also controlled by the polarity. Due to the interaction between the polar monomers from the droplets and the hydrophilic part of the surfactants, the specific area of the surface occupied by a surfactant molecule is higher for the polar monomer droplets [42–46]. At constant monomer and surfactant concentration the proportion of the surfactant not bound to the monomer droplets surface is higher in the case of polar monomers. This statement is valid for polymers of different polarities [21, 42, 45, 47–50]. Thus, for more polar monomer and polymer systems, the amount of surfactant attached to the interface is lower than for lower polarity systems.

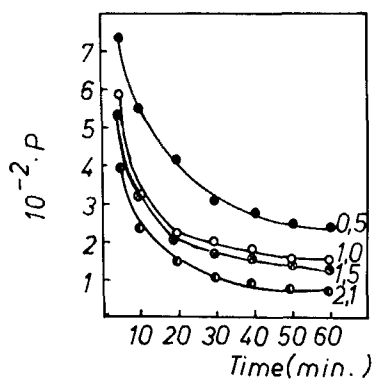
Figure 1 shows the case of systems with the VAc/DBM mixture; these systems exhibit a smaller amount of dissolved surfactant in the water phase because a larger part of it is fixed onto the monomer or at the copolymer/water interface. Owing to the lower concentration of water-solubilized surfactant which can react with the initiator, its decomposition rate is lower for the copolymerization systems.

The smaller rate of copolymer formation as compared to that of homopolymerization is probably due to the lower reaction rate of DBM [51]. Available literature data on reactivity rates are controversial [51]. In this contribution we employed a VAc/DBM ratio which enhances the reactivity of the rather sluggish DBM. To establish a correlation between the two reactions, i.e., polymerization and decomposition of the initiator, a P value (initiator productivity) was calculated, representing the ratio of the amount of polymer over that of decomposed initiator at a given reaction time; that is, polymer formed (in grams) while 1 g KPS is decomposed. The results obtained are shown in Figs. 2 and 3.

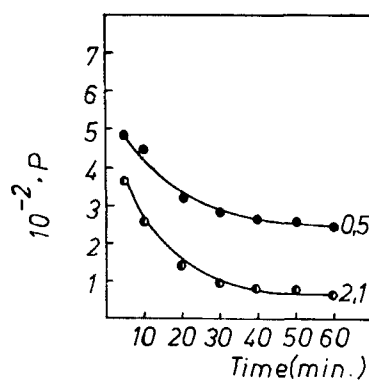
The results are obvious: the amount of polymer yielded by 1 g of decomposed KPS is always highest at the beginning of the process. The occurrence of a high rate of the initiator decomposition even when the polymerization reaction has declined results in a decrease of initiator productivity owing to side reactions. The lowest productivity (that is, the maximum level of the side reactions for initiator splitting) is obtained at maximum initiator concentrations.

The P values for the two concentrations of the emulsifier are not significantly different for homopolymerization (Fig. 2). In the case of copolymerization, the P values are higher at the lowest concentration of the surfactant (Fig. 3). These results show that the decline of the P value with time is accounted for by KPS–surfactant interactions. The polyethoxylated chain of the emulsifier is sensitive to the attack of the persulfate-type initiator [52].

The experimental results, especially the amounts of the polymer formed and the initiator decomposed, supply some information regarding the initiation effi-



a.

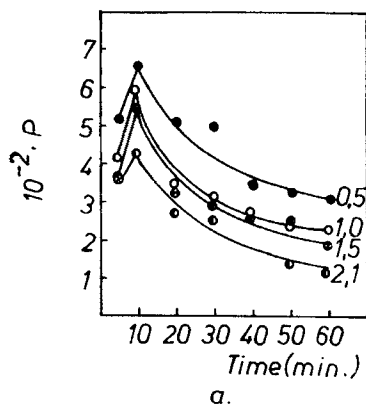


b.

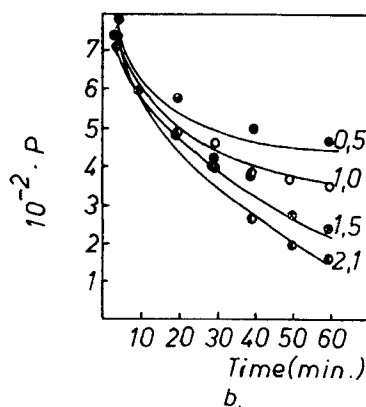
FIG. 2. Time evolution of the P value at various initiator concentrations [monomer, VAc; $[E]_0 = 5.8$ (a); 3.7 (b) g/100 mL H_2O ; $[KPS]_0$ (g) is specified on each trace].

ciency, provided that the degree of polymerization of the polymer is known. In this respect, we tried to separate the emulsifier from the polymer by water extraction. The resulting polymer was dried and extracted again with benzene in order to obtain polymers whose molecular weights could be accurately determined. In case (a) of Figs. 2 and 3, the fraction extracted in water was much lower than the amount of emulsifier initially fed in. The weight of the benzene-soluble fraction exceeds the theoretical amount of the polymer, showing that this fraction contains a considerable amount of chemically bound surfactant (Fig. 4). Because no differences between experiments with various initiator coefficients were noticed, all results were plotted on the same diagram.

Earlier investigations of the emulsion polymerization of vinyl acetate in the presence of some protective colloids have evidenced monomer grafting on colloid chains [3, 53-55]. The variance of the data in Fig. 4 in the presence of protective colloids at conversions over 60% indicates that the water-soluble fraction was smaller than the amount of the dispersion stabilizer and decreased continuously with the progress of polymerization. An increase of the water-soluble fraction as



a.



b.

FIG. 3. Time dependence of the P value for various initiator concentrations [monomer, VAc/DBM = 60/40; $[E]_0 = 5.8$ (a); 3.7 (b) g/100 mL H_2O ; $[KPS]_0$ (g) specified on each trace].

presented by Fig. 3 can originate only from splitting of the polyethoxylated chain of the surfactant [52], an assumption also supported by the simultaneous decrease of the insoluble fraction.

This suggests that the intense transfer reaction to the surfactant occurring in the polymerization system results in the formation of several poly(vinyl acetate) chains grafted and crosslinked on the emulsifier chain. The reduction of VAc concentration after 60% monomer conversion and the presence of unreacted initiator favors the interaction between KPS and the surfactant chain. These reactions between KPS and the surfactant ensure a higher splitting rate of the initiator than that observed in pure water.

The benzene-soluble fraction contains polymer and surfactants. Its intrinsic viscosity depends both on the molecular weight of the poly(vinyl acetate) chains grafted on the surfactant chains and on its composition. Such measurements cannot be used to establish the initiation efficiency. In the case of copolymers, the slope of plots of η_{sp}/c versus c is negative. This behavior is evidence of an advanced degree

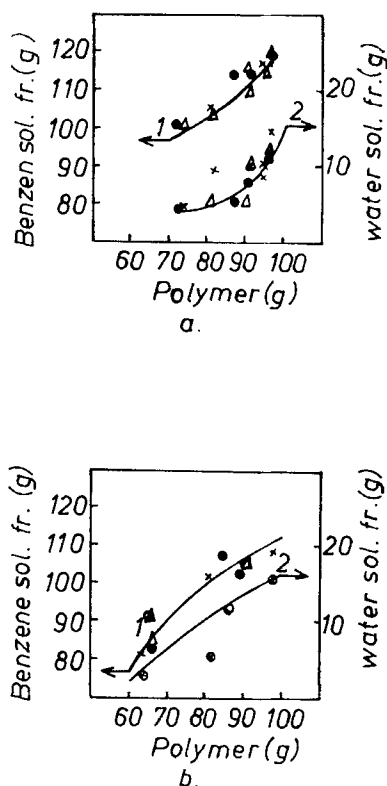


FIG. 4. Increase of benzene-soluble fraction (1) and of water-soluble fraction (2) vs polymer obtained (a, VAc; b, VAc/DBM = 60/40; $[E]_0 = 5.8$ g/100 mL H_2O ; $[KPS]_0 = 0.5$ – 2.1 g).

of branching [56] due to higher monomer grafting on the surfactant chain. For copolymers, the benzene-soluble fraction is smaller owing to the increase of the insoluble polymer fraction, demonstrating the higher probability for formation of grafted and crosslinked compounds in this case.

The P value for copolymers is higher than for homopolymers (Figs. 2 and 3). Taking into account that the amount of decomposed persulfate is lower for copolymers, it turns out that the splitting of surfactant chains is less probable. Thus, all experimental data support the idea that the degree of branching increases for copolymers.

At the end of the batch stage, both monomer and initiator conversions depend strongly on the amount of initiator [1]. The variation of polymer formed and of initiator decomposed presented in Figs. 5 and 6 retains the normal behavior of semicontinuous processes [3–5]. Earlier in the process the polymer is formed at a lower rate; therefore, the concentration of the residual monomer increases markedly and polymerization is slow. When the amount of polymer has reached a significant value, the rate of polymerization begins to increase and there is a linear dependence in time between the polymer and the amount of monomer continuously introduced.

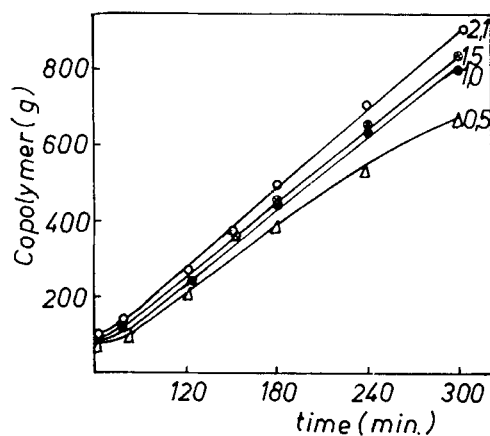


FIG. 5. The increase of the amount of polymer during the continuous addition stage (VAc/DBM = 60/40; $[E]_0 = 3.7$ g/100 mL H_2O ; $[KPS]_I = [KPS]_{II}$ specified on each curve).

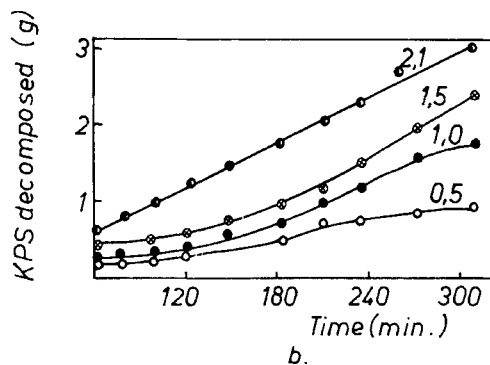
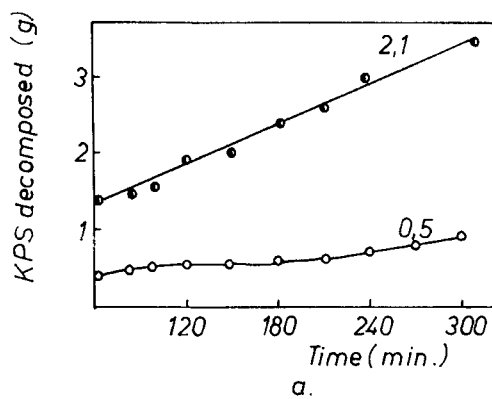


FIG. 6. Time dependence of the amount of decomposed initiator during the continuous addition stage [monomer, VAc (a); VAc/DBM = 60/40 (b)]; $[E]_0 = 3.7$ g/100 mL H_2O ; $[KPS]_I = [KPS]_{II}$ specified on each curve].

When a reduced amount of initiator is used, a normal decrease in polymer concentration and an increased amount of unreacted monomer are observed. The latter raises the amount of surfactant attached to the monomer-polymer particles, bringing about a reduction in the decomposition rate of the initiator. In case a larger amount of surfactant can be attached by grafting or crosslinking, the increase of monomer concentration accounts for enhanced blocking of the polyethoxylated polar chain by monomer molecules. This fact reduces the probability of KPS-surfactant interaction. For lower initiator concentrations, the time dependence of the amount of decomposed KPS is no longer linear. In this case, toward the end of the process, higher decomposition rates were recorded together with a diminished concentration of unreacted monomer and an increased amount of polymer. To our knowledge this result has not been reported previously, and it may explain the oscillation phenomena occurring in the semicontinuous and continuous processes [3-5, 48, 50, 57, 58].

The initiator conversion is not complete in any of the cases studied.

The data obtained suggest that variation of the initiator concentration entails productivity changes. Surfactant-initiator reactions lead to grafted and crosslinked copolymer and to emulsifier chain cleavage.

CONCLUSIONS

Due to selective interactions occurring between surfactants and monomers or polymers, decomposition of potassium persulfate used as the initiator is smaller in the presence of dibutyl maleate, the less polar monomer. The initiator productivity, defined as grams of polymer resulting from 1 g of decomposed initiator, decreases both with time and in the case of higher initial concentrations of initiator.

Side reactions between the surfactant and the initiator account for the observed grafting of the resulting polymer on the surfactant chain.

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