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# INFLUENCE OF INITIATOR TYPE ON THE LATEX PARTICLES SIZE IN EMULSION COPOLYMERIZATION OF STYRENE WITH BUTYL ACRYLATE

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**Key Words:** Emulsion copolymerization; Latex particles size; Styrene; Butyl acrylate; Water-insoluble initiator; Oxidized polypropylene

## ABSTRACT

Styrene (St) and butyl acrylate (BA) copolymer latexes were synthesized using two polymerization systems with different initiators. In System I a water-soluble initiator ( $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ ) was used. System II contained hydroperoxide groups bound to water-insoluble oxidized isotactic polypropylene (OPP) powder combined with the  $Fe^{2+}$  / ethylenediaminetetraacetic acid activator. The size of PSt/PBA latex particles ( $\bar{D}$ ) of the synthesized copolymer latexes was determined. The dependence of  $\bar{D}$  and surface tension was studied as a function of monomer conversion. It was found that the above parameters are dependent

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on the type of initiation system employed. In System II, larger latex particles are formed of increasing size as a function of monomer conversion. Smaller particles are produced in System I, and their size is almost unchanged during polymerization.

## INTRODUCTION

Water-based emulsion coatings have several advantages compared with organic solution-based paints. They improve the working environment in the production plant and on the application site; they reduce the risk of fire, decrease the cost of coating, and improve the standards for occupational health and safety [1]. Therefore, substantial efforts have been made to develop water-based emulsion coatings for a variety of industries. There exists a big market for polymeric water dispersions and emulsions for indoor and outdoor house applications. In the automobile industry it has become common to use water based-emulsion primers applied by electrocoating [2]. Waterborne coatings require surfactants in order to achieve low dynamic surface tension. This factor is important in order to prevent defects on formed films such as retraction, craters, and bubbles [3]. The film formation process of water-based emulsion coatings has been intensively studied by modern investigation techniques [4-7].

Increasing attention has been paid recently to the synthesis [8, 9] and study of the properties of styrene (St) and butyl acrylate (BA) dispersions. This has also been documented by the increasing numbers of patents issued worldwide focusing on PSt/PBA dispersions. This growing interest is caused mainly by the increasing industrial importance and ecological friendliness of water-based dispersions [6, 10].

In our previous paper [11] we studied the kinetics of emulsion copolymerization of St with BA using a conventional initiator ( $K_2S_2O_8$ ) and an untraditional water-insoluble initiator — hydroperoxides of oxidized isotactic polypropylene powder (OPP). We determined the reactivity ratios and molecular-weight characteristics of St/BA copolymers. It was found that the differences in reactivity ratios found for both systems are small. However, the  $\bar{M}_w$  value of PSt/PBA copolymers prepared in the system with OPP is much higher than the value for copolymers prepared with  $K_2S_2O_8$  initiator.

Based on these earlier results [11], we investigated the influence of initiator type on the latex particles size of PSt/PBA latexes. At the same time the relationship between changes of latex particles size as well as the surface tension as a function of conversion were studied.

## EXPERIMENTAL

### Materials

Styrene (Kaučuk Kralupy), stabilized. The stabilizer was removed by repeated washing with a 10% NaOH solution in a separatory funnel. The monomer was washed with water, and after drying was distilled under vacuum in a nitrogen atmosphere.

Butyl acrylate (Chemical Works Sokolov). Twice vacuum distilled under nitrogen.

Isotactic polypropylene (Slovnaft Bratislava). Powder with particles whose size was less than 0.3 mm, average viscosity number 340 mL/g, loose weight 134 g/L. The atactic residues were removed by a 10-time extraction with boiling *n*-heptane. The hydroperoxide concentration was determined by iodometry [12].

$K_2S_2O_8$  (Lachema Brno). This was used as a water solution with a concentration of  $9 \times 10^{-2}$  mol/L.

$Na_2S_2O_4 \cdot 2H_2O$ ,  $FeSO_4 \cdot 7H_2O$ , and disodium salt of ethylenediaminetetraacetic acid (EDTA) (all from Lachema Brno). These were used as water solutions with a concentration of  $4 \times 10^{-2}$  mol/L and were kept under a nitrogen atmosphere.

Emulsifiers. Mersol H [ $CH_3(CH_2)_{14}ONa$ ] (Leunawerke Merseburg), ionic type, and Slovasol 2340 (Chemical Works Nováky) [ $CH_3(CH_2)_{23}O(C_2H_4O)_{29}C_2H_4OH$ ], nonionic emulsifier, were used as water solutions with a concentration of 0.14 mol/L. The oxygen was removed from the solutions before use by boiling in a nitrogen atmosphere.

Solvents (*n*-heptane, acetone, methanol) (Lachema Brno). These were used as received.

## Procedures

### Copolymerization of Monomers

The emulsion copolymerizations of St and BA were performed in a glass reactor equipped with a mechanical stirrer, nitrogen inlet and outlet, and a rubber-septum-closed sampling neck. The temperature of copolymerization was 40°C and the rate of stirring was 300 rpm.

Two different initiating systems were used for copolymerizations. In both cases a constant volume of emulsion (80 mL) and a constant volume ratio of water phase to monomers were used. The composition of both polymerization systems is given in Tables 1 and 2.

A detailed description of the polymerization procedure is given in our previous paper [11]. The course of copolymerization was followed at certain time intervals

TABLE 1. Composition of System I for the Copolymerization of Styrene with Butyl Acrylate

	Volume, mL	Concentration, mol/L <sub>emulsion</sub>
Water phase:		
Initiator ( $K_2S_2O_8$ )	12	$1.37 \times 10^{-2}$
Activator ( $Na_2S_2O_4 \cdot 2H_2O$ )	4	$1.99 \times 10^{-3}$
Emulsifiers: Slovasol 2430	16	$2.90 \times 10^{-2}$
Mersol H	16	$2.90 \times 10^{-2}$
Organic phase:		
Monomers: Styrene <sup>a</sup>	16	
Butyl acrylate	16	

<sup>a</sup>The molar ratio of styrene in the monomer feed was  $f_{St} = 0.553$ .

TABLE 2. Composition of System II for the Copolymerization of Styrene with Butyl Acrylate

	Amount, g	Concentration, mol O <sub>2</sub> /kg PP
Solid phase:		
Initiator, OPP	1.6 <sup>a</sup>	1.9 × 10 <sup>-2</sup>
	Volume, mL	Concentration, mol/L <sub>emulsion</sub>
Water phase:		
Activators: FeSO <sub>4</sub> ·7H <sub>2</sub> O	3.6	1.79 × 10 <sup>-2</sup>
EDTA	3.6	1.79 × 10 <sup>-2</sup>
Emulsifiers: Slovasol 2430	16	2.90 × 10 <sup>-2</sup>
Mersol H	16	2.90 × 10 <sup>-2</sup>
Water	8.8	
Organic phase:		
Monomers: Styrene <sup>b</sup>	16	
Butyl acrylate	16	

<sup>a</sup>The concentration of hydroperoxides was determined by iodometry.

<sup>b</sup>The molar ratio of styrene in the monomer feed was  $f_{St} = 0.553$ .

by taking a small aliquot (about 1 mL) of the emulsion. The styrene/butyl acrylate copolymer was precipitated from the samples obtained in an excess of methanol, filtered on a frit, washed with water, washed with methanol, and then dried. The conversion of monomers was estimated from the known weight of comonomers in the mixture. The conversion of monomers (in weight %) was calculated according to equation:

$$\text{Conversion} = \frac{w_p w_e}{w_v w_m} \times 100 \quad (\text{wt}\%)$$

where  $w_p$  is the weight of precipitated polymer

$w_e$  is the weight of emulsion sample

$w_v$  is the sum of weights of all components of polymerization system

$w_m$  is the weight of monomers in the reactor feed

The samples of emulsions for surface tension measurements and determination of particle size were stabilized by the addition of hydroquinone.

## Characterization

### Surface Tension Measurements

The surface tension measurements of copolymer latexes were performed by a tensiometric method on a Tensiometer Lauda (Mesgerätwer Lauda). The method is based on the separation of a ring made from an alloy of platinum and iridium from

the surface of the measured liquid. The force required for the separation of the ring from the surface is proportional to the surface tension  $\gamma$ .

### Particles Size Determination

Two independent methods were used for particle size determination: light scattering and transmission electron microscopy.

The light-scattering measurements were carried out on a Particle Sizer, Model BI-90 (Brookhaven Instruments Corporation). The method is based on the intensity of scattered light after it has gone through a diluted dispersion solution. A He/Ne laser was used as the light source. The measurements are reliable for dispersion particles in the range from 5 nm to 5  $\mu\text{m}$ .

The microscopic measurements were performed on an electron microscope BS-500 (Tesla Brno) at a magnification of  $8000\times$ . The samples were prepared by impregnating a collodium-film covered copper screen with the studied dispersion. After the image of the sample was enlarged, the size of 150 to 300 particles was measured. The image of a polystyrene standard was superimposed at the same magnification. Using the average size of standard particles  $\bar{D}_{\text{NS}}$ , the average size of the prepared latex particles  $\bar{D}$  (in nm) was calculated according to

$$\bar{D} = \frac{a}{b} \bar{D}_{\text{NS}}$$

where  $a$  is the arithmetic mean of particle sizes of the sample (in nm)

$b$  is the arithmetic mean of particle sizes of the standard (in nm)

## RESULTS AND DISCUSSION

The changes of surface tension for water solutions of the two surfactants—ionic Mersol H and nonionic Slovasol 2430—were studied as a function of increasing emulgator concentration (Fig. 1). The critical micellar concentration (CMC) was determined at  $25^\circ\text{C}$  [13] from the bending point on the curves. For the water solution of Slovasol 2430, the CMC is  $1.35 \times 10^{-4} \text{ mol/dm}^3$  (which corresponds to  $0.18 \text{ g/dm}^3$ ), and for Mersol H,  $\text{CMC} = 1.79 \times 10^{-3} \text{ mol/dm}^3$  (which is  $0.55 \text{ g/dm}^3$ ). The differences in CMC values of the emulsifiers used can be related to other factors. One factor can be the different chemical structure and end-groups of nonionic Slovasol 2430 [formula  $\text{CH}_3(\text{CH}_2)_{23}\text{O}(\text{C}_2\text{H}_4\text{O})_{29}\text{C}_2\text{H}_4\text{OH}$ ] and ionic Mersol H [formula  $\text{CH}_3(\text{CH}_2)_{14}\text{ONa}$ ]. The length of the hydrophobic alkyl group  $-(\text{CH}_2)_x-$  in the Mersol H chain and the contribution of the hydrophilic  $-(\text{C}_2\text{H}_4\text{O})-$  segments in the Slovasol 2430 molecule play an important role. These factors can have an influence not only on the surface area of the emulsifier molecules taken on the surface of micelles but also on the ability to form the micelles effectively. This is why nonionic and ionic emulsifiers were used in combination [13].

Compared with the data in Tables 1 and 2, it is clear that the starting emulsifier concentrations for the copolymerization of styrene with butyl acrylate in initiation System I ( $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) and System II ( $\text{OPP-Fe}^{2+}/\text{EDTA}$ ) are many times higher than the CMC. In both cases the emulsifier plays an important role during copolymerization.

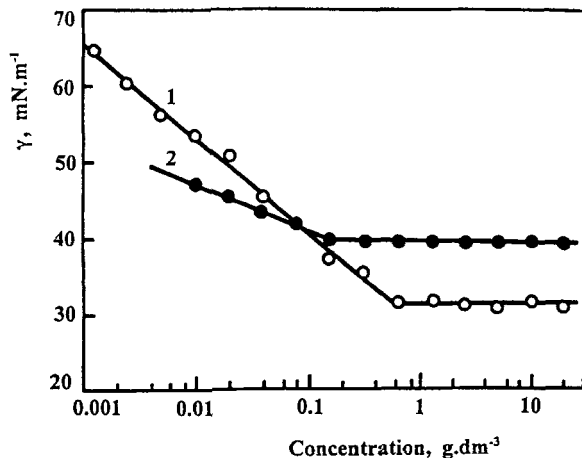


FIG. 1. Dependence of surface tension  $\gamma$  of water solutions of emulsifiers Slovasol 2430 (Line 1) and Mersol H (Line 2) as a function of concentration at 40°C.

A study of surface tension ( $\gamma$ ) as a function of the conversion of St and BA (Figs. 2 and 3) showed that free emulsifier is quickly consumed in the polymerization system, which can be assumed from the course of Curve 2 in both figures. From the lower values of  $\gamma$  in the system with OPP it can be deduced that the isotactic PP powder with its attached hydroperoxidic initiating groups requires a part of the emulsifier for the wetting of the solid PP surface. This allows the monomers and activator to come into close contact with the hydroperoxidic initiat-

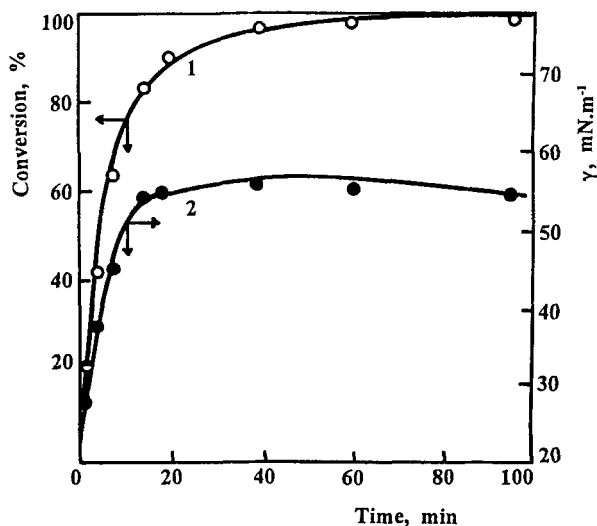


FIG. 2. Dependence of conversion of monomers (Line 1) and surface tension  $\gamma$  (Line 2) as a function of copolymerization time for St and BA in the emulsion polymerization System I with  $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ .

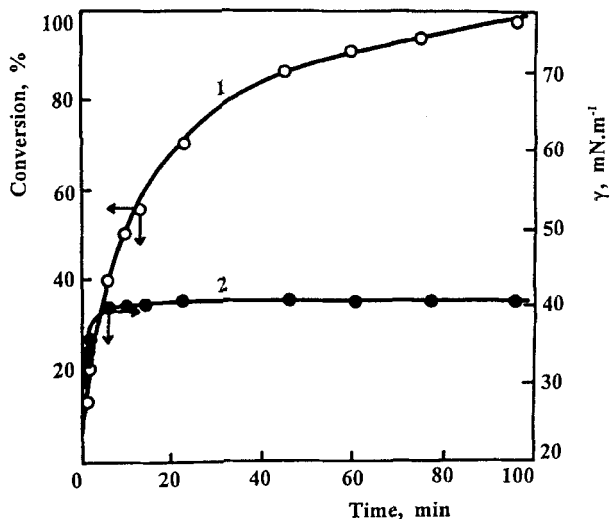


FIG. 3. Dependence of conversion of monomers (Line 1) and surface tension  $\gamma$  (Line 2) as a function of copolymerization time for St and BA in the emulsion polymerization System II with OPP-Fe<sup>2+</sup>/EDTA.

ing groups. The concentration of free emulsifier is substantially diminished by this. The relatively lower content of free emulsifier in System II can be one of the reasons why the particles size in this polymerization is high compared with System I using the soluble K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> initiator (Fig. 4).

From the results presented in Fig. 4 it is clear that the particles size of St-BA copolymer latex with OPP initiator increases with conversion. The results were

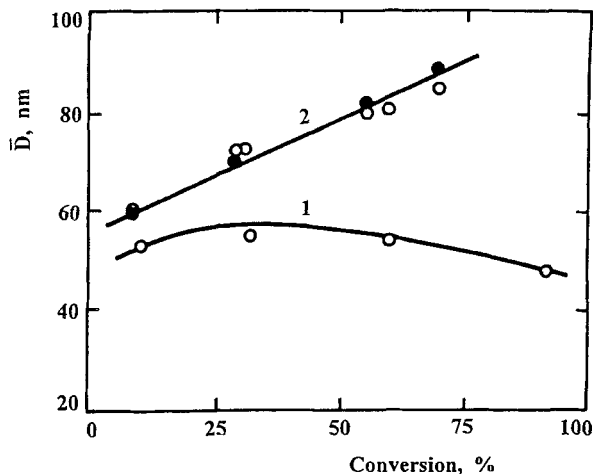


FIG. 4. Dependence of the latex particle size  $\bar{D}$  as a function of conversion of monomers in copolymerization of St with BA in the presence of System I (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) (Line 1) and System II (OPP-Fe<sup>2+</sup>/EDTA) (Line 2). The particles size was measured by light scattering (○) and by transmission electron microscopy (●).



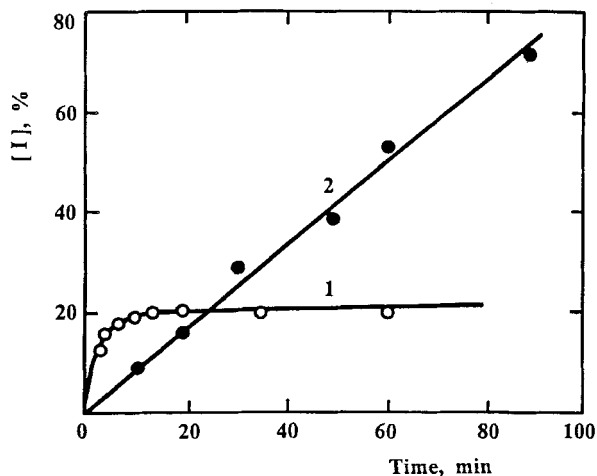
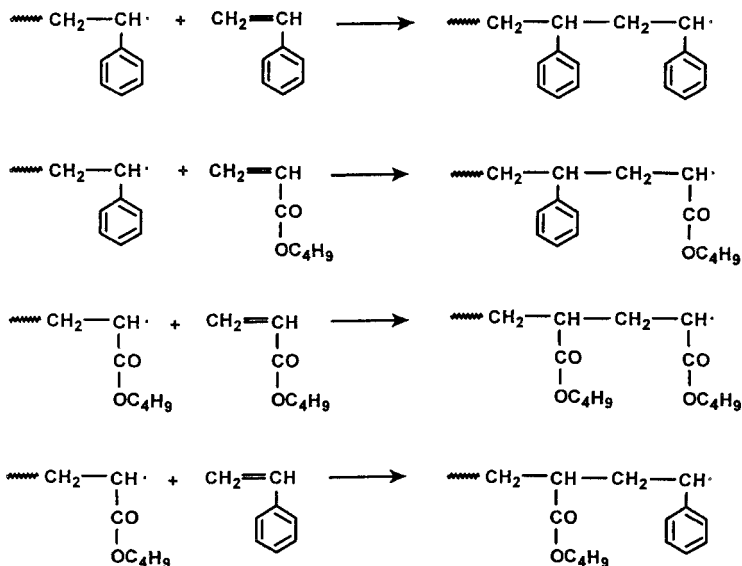
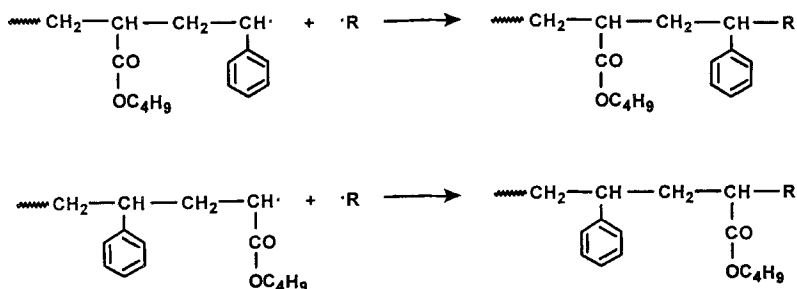


FIG. 5. Dependence of amount of initiating groups [I] decomposed as a function of time in the emulsion copolymerization of St/BA using: (1)  $K_2S_2O_8$ /Slovasol 2430, (2) OPP/ $Fe^{2+}$ /EDTA/Slovasol 2430.

confirmed by two independent methods: light scattering and transmission electron microscopy. This finding is contrary to data obtained for the copolymerization using  $K_2S_2O_8$  where the particles size first increases and later slightly decreases. These results are related to the fact that in the system with OPP, the hydroperoxides decompose primarily only at the beginning of the copolymerization reaction (predominantly during the first 20 minutes [11]). The situation in the system with



SCHEME 1.



SCHEME 2.

$\text{K}_2\text{S}_2\text{O}_8$  is different because the peroxidic groups decompose during the whole polymerization period (Fig. 5). In polymerization System II the primary radicals are not formed from the initiator during the whole copolymerization, and therefore they cannot enter into the polymer-monomer particles and take part in the termination reactions according to the Smith-Ewart theory [14].

We assume that after initiation with the primary radical  $\text{R}\cdot$  the propagation reactions lead to the formation of four types of growth radicals (Scheme 1). They can be formed in both Systems I and II with a similar mechanism. The absence of two types of termination reactions (Scheme 2) in System II allows the propagating radicals in the latex particles to reach a longer length. We think that this is the main reason why the latex particles in System II are larger than those in System I.

## CONCLUSION

From the results presented it can be concluded that the particle size of styrene-butyl acrylate latexes is dependent on the initiation system. The absence of termination reactions in System II with hydroperoxides bonded to oxidized PP powder allows the propagating radicals to grow longer. It can be assumed that this is the main reason why the latex particles in System II reach a larger size than those in System I with a water-soluble  $\text{K}_2\text{S}_2\text{O}_8$  initiator. It has been also shown that the size of PSt/PBA latex particles increases in System II as a function of monomer conversion. This is contrary to System I, where termination reactions with the primary radicals formed from  $\text{K}_2\text{S}_2\text{O}_8$  initiator can proceed during the whole period of copolymerization of St with BA.

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