The Influence of Initiator Type on Emulsion Copolymerization of Styrene with Butyl Acrylate

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ABSTRACT

The emulsion copolymerization of styrene (St) and butyl acrylate (BA) was studied in 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 hydroperoxidic groups bound to water-insoluble oxidized polypropylene (OPP) powder in combination with the Fe^{2+}/ethylenediaminetetraacetic acid activator. The influence of the initiator type on the overall rate of copolymerization, reactivity ratios, and on the molecular-weight characteristics of St/BA copolymers was studied. The reactivity ratios were $r_{St} = 0.72$, $r_{BA} = 0.27$ for System I; and $r_{St} = 0.79$, $r_{BA} = 0.12$ for System II. It was found that the presence of initiation centers on the surface of OPP in System II was responsible for the lower values of the overall rates of polymerization. However, the molecular weights of St/BA copolymers were much higher in System II than in System I with the water-soluble initiator.

INTRODUCTION

The emulsion copolymerization of styrene (St) with butyl acrylate (BA) is studied in detail because of its industrial importance. The kinetics of copolymerization of St with BA was the interest of several papers [1, 2]. The influences of initiator, emulsifier, and monomer concentrations on the rate of copolymerization were studied [3]. The characteristic properties of emulsions as well as the molecular weights of St/BA copolymers were also investigated [4]. The most often used are dissociation initiators {$K_2S_2O_8$ and $(NH_4)_2S_2O_8$} or redox systems ($K_2S_2O_8/Na_2S_2O_5$).

Conventional emulsion systems allow the Harkins–Smith–Ewart theory [5] to be applied. They are characterized by the formation of radical species in the water phase with the monomers present in the organic phase.

In addition to the conventional water-soluble initiation system for emulsion copolymerization, we used a nontraditional initiator, oxidized isotactic polypropylene (OPP) powder. We reported earlier [6] that the hydroperoxidic groups on the surface of PP powder can be used for the initiation of the emulsion polymerization of styrene in the presence of an amine activator. This type of initiator was also applied for the synthesis of block copolymers of styrene with methyl methacrylate [7], *p-tert*-butyl styrene [8], and maleic anhydride [9].

The initiator, oxidized polypropylene powder, is characterized by:

1. Relative high specific surface ($5.6 \ m^2/g$)
2. Insolubility in both the water and organic phases of an emulsion polymerization system
3. Fast decomposition of the hydroperoxides bound to the surface of OPP in the initial stages of emulsion polymerization in the presence of an activator [10]

We studied the emulsion copolymerization of styrene with butyl acrylate initiated by OPP in the presence of an activator. The results obtained were compared to a conventional system with a water-soluble initiator. The objective of this work was to study the influence of initiator type on the rate of copolymerization of St and BA, the values of the reactivity ratios, and the molecular weight characteristics of the St/BA copolymers.

EXPERIMENTAL

Materials

Styrene (Kaučuk Kralupy), stabilized. Pure monomer was prepared by repeated washing with a 10% NaOH solution, water, and, after drying, by vacuum distillation in a nitrogen atmosphere.

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

Isotactic polypropylene (Slovnaft Bratislava). Powder with a particle size of 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 by boiling *n*-heptane.

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

Na$_2$S$_2$O$_4$·2H$_2$O (Lachema Brno), used as a water solution with a concentration of 4 × 10^{-2} mol/L.

FeSO$_4$·7H$_2$O (Lachema Brno), used as a water solution with a concentration of 4 × 10^{-2} mol/L.

Disodium salt of ethylenediaminetetraacetic acid (EDTA) (Lachema Brno), used as a water solution with a concentration of 4 × 10^{-2} mol/L.

Mersol H [CH$_3$(CH$_2$)$_{14}$ONa] (Leunawerke Merseburg), ionic emulsifier, used as a water solution with a concentration of 0.14 mol/L. The oxygen was removed from the solution by boiling for 1 hour in an inert atmosphere.

Slovasol 2340 (Chemical Works Nováky) [CH$_3$(CH$_2$)$_{23}$O(C$_2$H$_4$O)$_{29}$C$_2$H$_4$OH], nonionic emulsifier, used as a water solution with a concentration of 0.14 mol/L. The oxygen was removed from the solution before use by boiling in a nitrogen atmosphere.

Water, twice distilled in a nitrogen atmosphere in a glass apparatus.

Solvents, *n*-heptane, acetone, methanol, methyl ethyl ketone (MEK) (Lachema Brno), used as received.

Procedures

Oxidation of PP and Hydroperoxides Determination

Oxidized isotactic PP was prepared by ozonolysis at room temperature in a glass fluidized bed reactor. The gas flow rate was 2 L/min, the concentration of ozone was 12 mg/L and the reaction time was 1 hour. The concentration of hydroperoxides in OPP powder was measured by iodometric titration [11]. The specific surface area of OPP (5.6 m^2/g) was measured by using the adsorption and the desorption of nitrogen on a FlowSorb 2300 (VA Brno).

Copolymerization of Monomers

The batch emulsion copolymerization of St and BA was 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 polymerization systems were used with different initiators. 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.

In System I, the solutions of emulsifiers were injected under nitrogen into the reactor followed by the monomers. After 15 minutes, when the reaction temperature was reached, the solutions of initiator and activator were added.

In System II, the OPP was first introduced into the reactor. The concentration of initiating groups was lower than in System I in order to keep the amount of the solid phase at a minimum level. The system was evacuated for a few times at 0°C and then flushed with nitrogen in order to remove oxygen. The solutions of emulsifiers, monomers, and water were injected through the septum. The reactor was heated to 40°C for 5 minutes, and the solution of activator was added.

The copolymerization was followed at certain time intervals by taking small aliquots (about 1 mL emulsion). In System I the sample was taken by syringe, in

TABLE 1.   Composition of Polymerization System I

	Volume, mL	Concentration, mol/L$_{emulsion}$
Water phase:		
Initiator ($K_2S_2O_8$)	12	1.37×10^{-2}
Activator ($Na_2S_2O_4 \cdot 2H_2O$)	4	1.99×10^{-3}
Emulgators: Slovasol 2430	16	2.90×10^{-2}
Mersol H	16	2.90×10^{-2}
Organic phase:		
Monomers: Styrene[a]	x	
Butyl acrylate		

[a]The molar ratio of styrene in the monomer feed was f_{St} = 0.121, 0.346, 0.553, 0.749, and 0.917.

System II by a probe with a glass frit which separated the emulsion from the PP powder. The styrene/butyl acrylate copolymer was precipitated from obtained samples in an excess of methanol, filtered on a frit, washed with water, methanol, and then dried. The conversion of monomers was calculated from the known weight of comonomers in the mixture. At the end of copolymerization the emulsion was separated from the PP powder by filtration on a fritted funnel (porosity, 20 μm). OPP was washed afterward with warm and cold water, methanol, and the powder

TABLE 2.   Composition of Polymerization System II

	Amount, g	Concentration, mol O_2/kg PP
Solid phase:		
Initiator, OPP	1.6	1.9×10^{-2}

	Volume, mL	Concentration, mol/L$_{emulsion}$
Water phase:		
Activator: $FeSO_4 \cdot 7H_2O$	3.6	1.79×10^{-2}
EDTA	3.6	1.79×10^{-2}
Emulgators: Slovasol 2430	16	2.90×10^{-2}
Mersol H	16	2.90×10^{-2}
Water	8.8	
Organic phase:		
Monomers: Styrene[a]	x	
Butyl acrylate	$32 - x$	

[a]The molar ratio of styrene in the monomer feed was f_{St} = 0.121, 0.346, 0.553, 0.749, and 0.917.

obtained was dried in vacuum. The weight increase, which may represent the grafted St/BA copolymer, was 0.9–2.1%.

Characterization

The composition of St/BA copolymers was estimated on the basis of elemental analysis performed on a CHN + O Analyser, Model 1102 (Carlo Erba, Milan). The results were compared to the composition obtained by refractive index increment measurements on a Brice Phoenix differential refractometer (Virtis Company, Gardiner, New York) of copolymer ν_{copol} and corresponding homopolymers ν_{St} and ν_{BA} in methyl ethyl ketone:

$$\nu_{copol} = \nu_{St}x_{St} + (1 - x_{St})\nu_{BA}$$

where x_{St} is the weight portion of styrene in the copolymer.

The molar portions of styrene (F_{St}) and butyl acrylate (F_{BA}) in the copolymer were calculated on the basis of the composition found for the copolymers.

The viscometric measurements of the copolymers were done in dioxane at 35°C and in methyl ethyl ketone at 25°C in an Ubbelohde viscometer. The limiting viscosity number $[\eta]$ of the copolymer was found after extrapolation of the following dependence to zero concentration:

$$\frac{\eta - \eta_0}{\eta_0 c} = [\eta] + k_H[\eta]^2 c$$

where η and η_0 are the flow times for the solution and the solvent, respectively
   c is the concentration of copolymer in g/dL
   k_H is the Huggins constant

The light-scattering measurements were carried out on a Photometer Sofica 4200 (Sociate Francaise Instruments) at 546 nm. The starting solution of copolymer in MEK had a concentration of 3.2×10^{-4} g/mL and was diluted four times with the solvent. The light-scattering measurements were performed between angles of 30 to 75° with increments of 5°. The apparent mass molecular weight of the copolymer, $\overline{M}_{w\,app}$, was obtained from the reduced intensity data of light scattering according to a known procedure [12].

RESULTS AND DISCUSSION

The influence of initiator type on the emulsion copolymerization of styrene with butyl acrylate was investigated in System I ($K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$) and System II (OPP-$Fe^{2+}$/EDTA). In both cases the copolymers were prepared with different starting ratios of St and BA in the monomer feed.

The conversion curves of the copolymerization of St with BA for a molar ratio of styrene of $f_{St} = 0.553$ for both initiation systems are shown in Fig. 1. Similar dependences were obtained for other copolymerizations when the f_{St} was in the 0.121 to 0.917 range. The overall rates of copolymerization R_p for both initiation systems were calculated from the stationary parts of the conversion curves (between
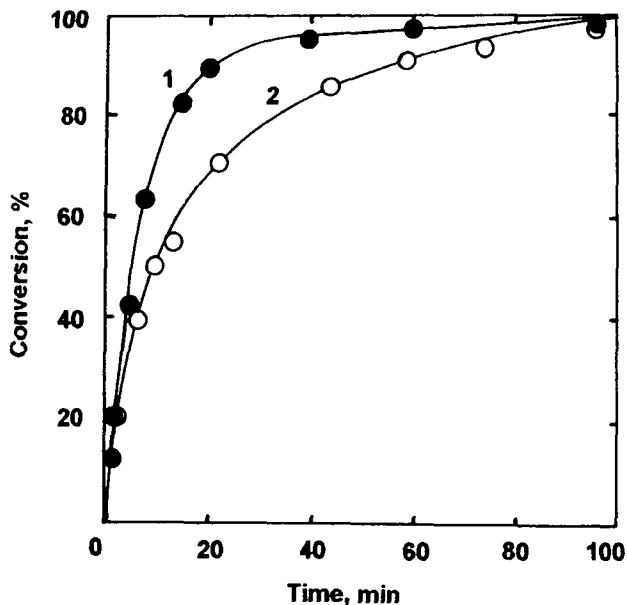
FIG. 1.   Conversion curves of emulsion copolymerization of St with BA ($f_{St} = 0.553$) at 40°C in the systems (1) $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ and (2) OPP–Fe^{2+}/EDTA.

20 and 40% of conversion). The dependence of the copolymerization rate as a function of the molar ratio of styrene in the monomer feed is shown in Fig. 2.

In both systems the rate of copolymerization of St with BA is inversely proportional to the styrene concentration in the starting monomer feed. The experiments showed that the water-soluble initiating system produced higher rates of copolymerization at all ratios of St in the monomer feed compared to the OPP–Fe^{2+}/EDTA system. Here, the hydroperoxidic groups are present on the surface of the polymer powder. The differences in the rates of copolymerization in emulsion systems can be attributed to a higher initiator concentration in System I compared with System II, and also to other factors.

This work focuses attention on the influence of the initiator used, mainly on the position of the initiator in the emulsion system. It is known that when a water-soluble initiator is used, the formation of primary radicals proceeds in the water phase of an emulsion polymerization system. According to classical micellar theory [5], the initiator radicals enter the micelles swollen with the water-insoluble monomer, and it is there that polymerization starts. Butyl acrylate is partially soluble in water (11 mM at 25°C), and initiation also takes place in the water phase. Therefore, polymer macromolecules can be formed by homogeneous nucleation [13]. An increase in concentration of partially water-soluble BA in the monomer feed can have a positive influence on the overall rate of copolymerization.

The idea of the formation of polymer particles during the emulsion copolymerization initiated by the hydroperoxides of OPP is slightly different. We propose that the hydroperoxidic groups decompose on the surface of polypropylene in the thin layer of emulsifier solution. This solubilizes the monomers and at the same
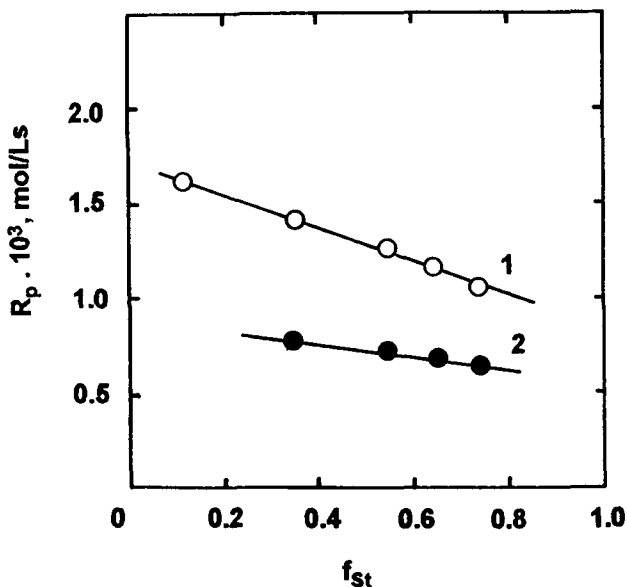
FIG. 2. The influence of the molar fraction of styrene in the mixture of monomers (f_{St}) on the rate of St/BA emulsion copolymerization (R_p) with (1) $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ and (2) OPP-Fe^{2+}/EDTA.

time wets the surface of OPP (Fig. 3). When the fast-growing copolymer chains reach a certain length after initiation, they leave the surface to form copolymer particles. This idea is supported by the presence of a small amount of grafted St/BA copolymer on the surface of the OPP particles at the end of copolymerization. That may also be the reason for the low utilization of these surface-bound hydroperoxides.
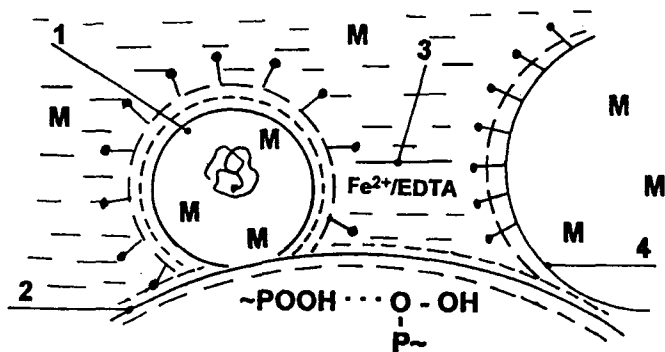

FIG. 3. Schematic representation of emulsion polymerization in the presence of hydroperoxides bonded to water-insoluble isotactic-oxidized polypropylene: (1) polymer particle, (2) surface of initiator, (3) water-soluble activator, (4) monomer droplet.
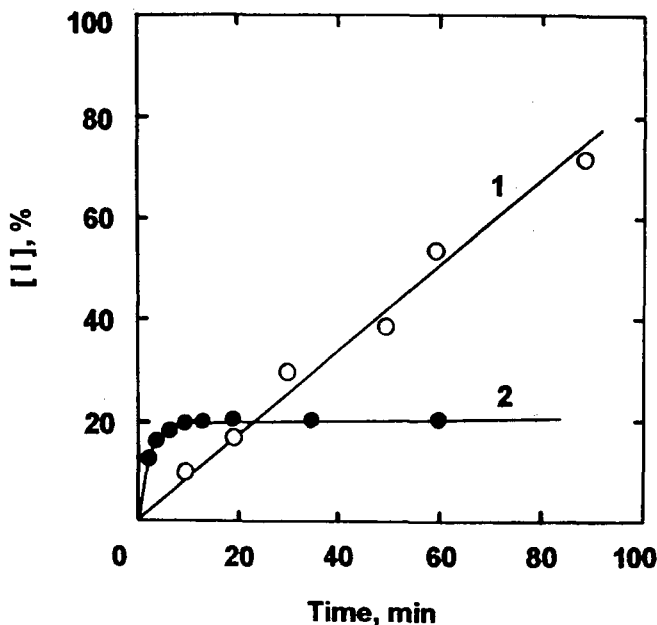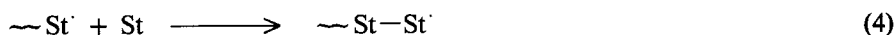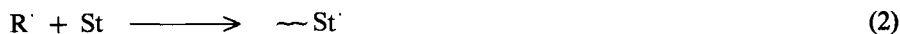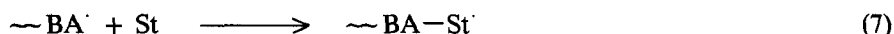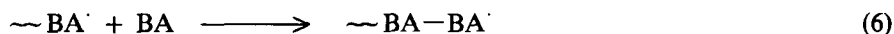
FIG. 4.   Amount of initiating groups [I] decomposed as a function of time in the emulsion copolymerization of St/BA using (1) $K_2S_2O_8$/Slovasol 2430 and (2) OPP/Fe^{2+}/EDTA/Slovasol 2430.

Earlier reports [6, 10] and our present results confirm that only a small part of the hydroperoxides of OPP are able to form radicals suitable for initiation of the polymerization reaction in the presence of activator and monomers (Fig. 4, Curve 2). The rest of the hydroperoxidic centers are left unutilized. The position of initiating groups in System II with their relatively lower concentration and restricted formation of primary radicals during the copolymerization of St with BA is responsible for the lower values of the overall rate of copolymerization. However, in System I the decomposition of water-soluble initiator proceeds during the whole copolymerization (Fig. 4, Curve 1).

Differences in the initiation step of radical copolymerization of St with BA in emulsion primarily influence the first three steps in the following reaction scheme which explains the formation of primary and monomer radicals.

$$R-R \longrightarrow 2R\cdot \tag{1}$$

$$R\cdot + St \longrightarrow \sim St\cdot \tag{2}$$

$$R\cdot + BA \longrightarrow \sim BA\cdot \tag{3}$$

$$\sim St\cdot + St \longrightarrow \sim St-St\cdot \tag{4}$$

$$\sim St\cdot + BA \longrightarrow \sim St-BA\cdot \tag{5}$$

$$\sim BA^{\cdot} + BA \longrightarrow \sim BA-BA^{\cdot} \tag{6}$$

$$\sim BA^{\cdot} + St \longrightarrow \sim BA-St^{\cdot} \tag{7}$$

The ability of St and BA to take part in propagation reactions (3)–(7) depends mostly on the reactivity of the monomers, the propagating radicals, and the local concentration of monomers in the reaction site. There is only a small influence of OPP on the propagation reaction. This can be deduced from the small differences in the copolymerization curves (Fig. 5) and from the values of the reactivity ratios.

The values of the reactivity ratios, calculated according to the Joshi–Joshi method [14], are not very different from the emulsion copolymerization of St with BA initiated by a water-soluble initiator ($K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$) and the OPP–$Fe^{2+}$/EDTA system:

$$r_{St} = 0.72, r_{BA} = 0.27 \quad \text{for System I}$$
$$r_{St} = 0.79, r_{BA} = 0.12 \quad \text{for System II}$$

It is assumed that in classical emulsion polymerization with a water-soluble initiator, termination proceeds by the reaction of a propagating radical with an initiator radical which enters the polymer particle. When hydroperoxides bound to the OPP are used, the probability of this type of reaction is restricted by the fact that the decomposition of hydroperoxides proceeds significantly only on the beginning (first 20 minutes) of the copolymerization (Fig. 4). In the later stages of copolymerization, the primary radicals are practically not formed. The polymerization
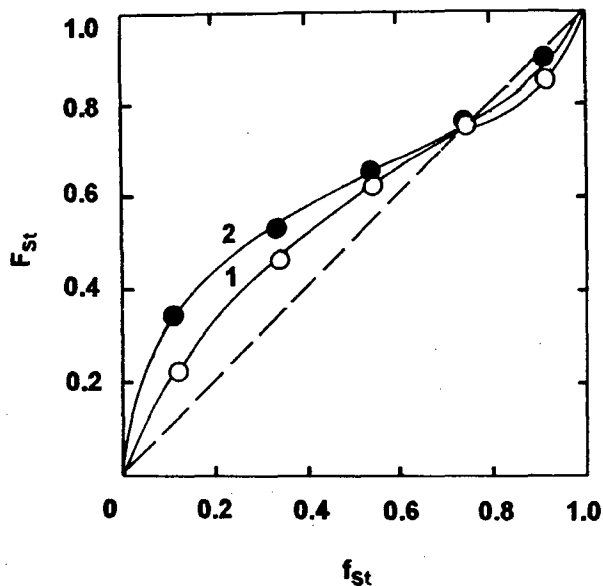

FIG. 5. Dependence of molar fraction of styrene in the copolymer (F_{St}) as a function of molar fraction of styrene in the monomer feed (f_{St}) for emulsion copolymerization of St/BA in the systems (1) $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ and (2) OPP–Fe^{2+}/EDTA.
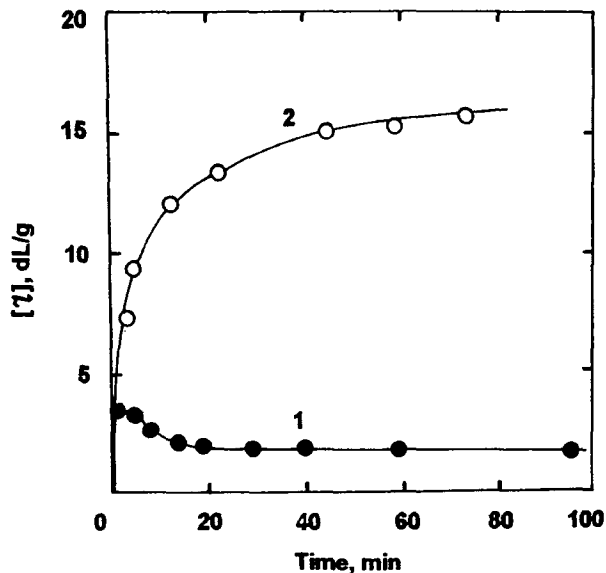
FIG. 6.   Dependence of the limiting viscosity number $[\eta]$ of St/BA copolymers (measured in dioxane at 35°C) as a function of copolymerization time in the emulsion with f_{St} = 0.553 using (1) $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ and (2) $OPP-Fe^{2+}/EDTA$.
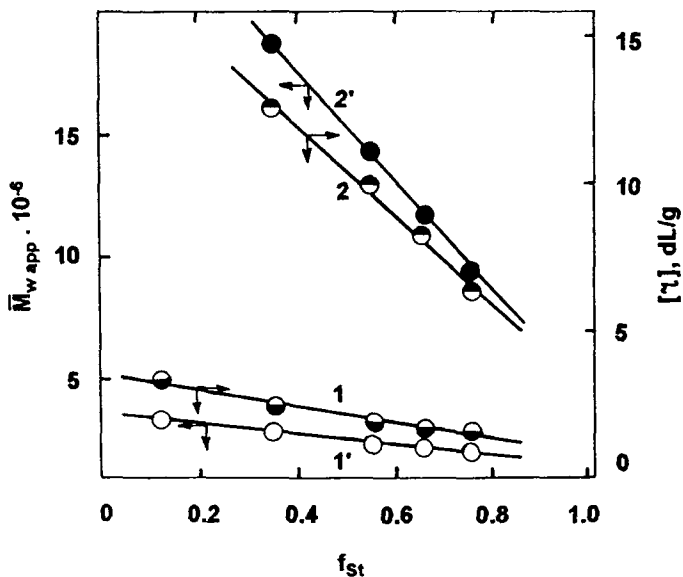

FIG. 7.   Dependence of the $\overline{M}_{w\,app}$ and $[\eta]$ (measured in MEK at 25°C) on the molar fraction of styrene in the monomer feed (f_{St}) for St/BA copolymers prepared by emulsion copolymerization using $(1,1')$ $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ and $(2,2')$ $OPP-Fe^{2+}/EDTA$.

proceeds by the long-living polymer radicals which are protected by the layer of emulsifier in the polymer particles. The decreased probability of termination with primary radicals in System II is expressed by an increase in the limiting viscosity number $[\eta]$ of the copolymer with the reaction time. The copolymers of St with BA prepared by System I have much lower values of $[\eta]$ which are basically independent on reaction time (Fig. 6). Similar results were obtained for copolymerizations with different St/BA feed ratios.

The molecular weights of St/BA copolymers with different compositions isolated at the end of the reaction were measured by the light-scattering method. It was found that $\overline{M}_{w\ app}$ of copolymers prepared in the OPP–Fe^{2+}/EDTA system are 4 to 5 times higher than for copolymers prepared in System I with a water-soluble initiator (Fig. 7). This is caused by the absence of primary radicals in System II during most of the copolymerization. The suppression of the termination reaction of the propagating polymer radicals leads in System II to the formation of copolymers with extremely high molecular weights. Preliminary results from particle size analysis of emulsions of St/BA copolymers have shown that in System II the particles of latex are bigger than in System I. A detailed analysis will be the subject of our next paper.

CONCLUSION

We found that the emulsion copolymerization of styrene with butyl acrylate is influenced by the initiator type, its position in the polymerization system, and the related mechanism of initiation.

In the case of a water-soluble initiator ($K_2S_2O_8$/$Na_2S_2O_4 \cdot 2H_2O$), decomposition of peroxide proceeds in the water phase throughout the copolymerization. In the OPP–Fe^{2+}/EDTA system, the hydroperoxides bound to the surface of OPP decompose almost exclusively in the initial stage of polymerization. This fact has a greater influence on the molecular weight characteristics of the St/BA copolymers than on the values of the reactivity ratios and the rate of copolymerization of St with BA.

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