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Kinetics of the styrene emulsion polymerization above cmc. II. Agitation effect on molecular weight

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Summary

The effect of stirring speed (SS) on the kinetics of styrene emulsion polymerization at 70ºC, using SDS as surfactant and KPS as initiator, was studied. The conversion (*x*) and weight average molecular weight (*Mw*) results are higher in the optimum SS range, which seems to be strongly dependent on the hydrodynamic characteristics of the reactor and the polymerization conditions. Above the optimum SS range, the number of particles and Mw are lower, therefore limited coagulation lead to a decrease in *Mw* caused by the increment of the free-radical entry frequency. These radicals not only come from the aqueous phase (oligomeric radicals), but also come from the radicals contained in the particles subject of coagulation (coagulative entry).

Introduction

Average molecular weight (*M*) and molecular weight distribution (MWD) are very important characteristics that have influence not only on the mechanical properties of the polymer formed by emulsion polymerization, but also on the film-formation process involved in many applications of polymer latexes.

On the other hand, stirred tank reactors are commonly used to perform emulsion polymerizations on laboratory, pilot plant and industrial scales. It is well recognized that agitation plays an important role on this process; however, its effect on *M* and MWD has been scarcely studied [1-3]. Most of the works focus on how agitation affects emulsification of monomer, mass transfer between droplets and particles, and coagulation (e.g. see [2,4,5] and references cited there in). Not to much attention has been paid on the effect of these issues on *M* and MWD.

In the present work, the kinetics of styrene emulsion polymerization at 70ºC, using SDS as surfactant and KPS as initiator was studied making emphasis on the effect of agitation on *M*.

Experimental

Materials

Distilled styrene monomer (Aldrich) and deionized water were used for all the reactions and the remaining materials were used as received. Sodium dodecyl sulfate (SDS, ≥99.0%, Fluka) and potassium persulfate (KPS, Aldrich) were used as surfactant and initiator, respectively. Nitrogen (Infra, México) ultrahigh purity grade (>99.999%) was used to remove oxygen from the reaction mixture. THF (HPLC grade, Aldrich) was the elution media in the GPC runs.

Equipment and instruments

Batch emulsion polymerizations were carried out in a cylindrical round-bottom glass reactor with jacket, sampling valve and four baffles plates located at 90º. The reactor diameter is 10 cm. The reaction temperature (T) was maintained by mean of a constant-temperature bath. Two types of impellers were used: PTFE half-moon blade (Aldrich) and Anchor. In both cases the impeller was located 1 cm from the bottom.
The samples were freeze-dried in a Labconco 6 Freeze Dry Freezone system. *MWD*s were obtained by size exclusion chromatography using a Hewlett-Packard instrument (HPLC series 1100) equipped with UV and refractive index detectors. A series of three Hewlett Packard PLGel columns were used: 10^3, 10^5, and 10^6Å.
Particle size was measured at 25 ºC and an angle of 90º in a Malvern 4700 dynamic light scattering (DLS) apparatus.

Polymerization

Before the polymerization was started, water, surfactant, and monomer were fed to the reactor; the stirrer speed was set at the desired value. T was increased from room temperature to 70ºC while nitrogen was passed through the reactor for 20 min.
To start the reaction, the initiator was dissolved in 10 g of deionized water and it was injected into the reactor.
Samples were withdrawn periodically from the reactor, short-sttoped with a 2% aqueous hydroquinone solution and freeze-dried. The weight of polymer was calculated by subtracting the known weights of surfactant and hydroquinone from the total weight of the freeze-dried sample.
For the GPC runs, the freeze-dried samples were extensively washed with deionized water to eliminate surfactant and freeze-dried again. The flow rate was 0.6 ml/min. The calibration curve was created from 10 monodisperse polystyrene standards with molecular weights in the range of 1.62×10^2 to $1.14\times\text{x}10^7$.
The following equation was used to calculate N from experimental data of conversion and particle size distribution:

$$N = \frac{6M_0 x}{\pi d_p \sum_i n_i D_i^3} \tag{2}$$

Where n_i is the number fraction of particles with unswollen diameter D_i, x is the fractional conversion of monomer and d_p is the polymer density. M_0 is the initial monomer concentration (g/cc water).

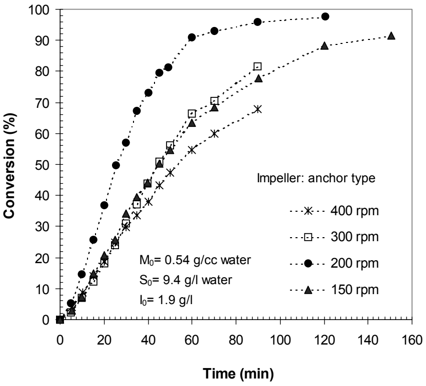

Figure 1. Effect of stirring speed on monomer conversion as function of time. Initial concentrations of monomer (M_0), surfactant (S_0) and initiator (I_0) are indicated in the figure.

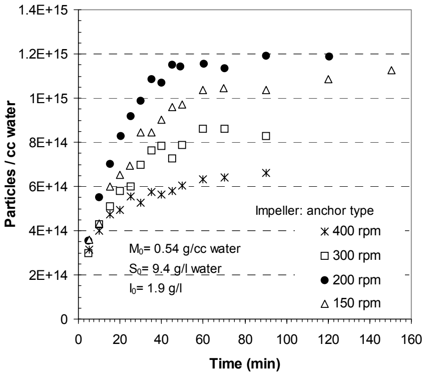

Figure 2. Effect of stirring speed on the number of particles as function of time for the conditions of figure 1.

Results and discussion

Figures 1 and 2 show the effect of the stirring speed (SS) on *x* and *N* as a function of time, respectively. It can be observed that in the SS range of 200-400 rpm, the smaller the SS the greater the rate of polymerization and *N*. When the SS is 150 rpm the opposite trend is obtained; that is, at a given time the *Rp* and *N* are smaller at 150 rpm than at 200 rpm. This indicates that for the system and reactor configuration used in this study the optimum SS is around 200 rpm.

It has been reported [1] that in the presence of well-purified nitrogen atmosphere *N* decreases at higher SS, as it was observed in the present work. Otherwise, in the presence of imperfectly purified nitrogen, high SS causes long retardation periods leading to greater values of *N* than in the situations without retardation periods [1,6]. Therefore, it is reasonable to assume that practically all the oxygen was removed from the polymerisations performed in this work by applying the procedure described in the experimental section.

Figure 3 shows the effect of SS on *N* as function of the monomer conversion. As can be observed in this figure, the trends obtained are the same than in Figure 2, except for the run at 150 rpm which data curve coincides with that performed at 200 rpm. This behavior is because [1] the SS is not enough to emulsify the monomer so that part of this monomer separates from the emulsion during interval II leading to a decrease in the rate of monomer transport to the particles where polymerization is taking place. During interval I, there is not significant phase separation because the surface of the monomer droplets is covered at the saturation value of the surfactant. In contrast, surfactant coverage diminishes during interval II because of the absence of micelles and the growth of polymer latex particles. This explains why at 150 and 200 rpm the same *N* was obtained at a given conversion but the Rp was slower at 150 rpm.

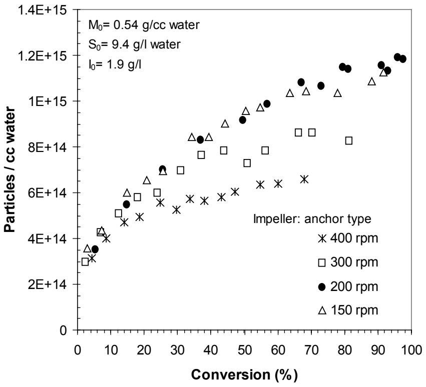

Figure 3. Effect of stirring speed on the number of particles as function of monomer conversion for the conditions of Figure 1.

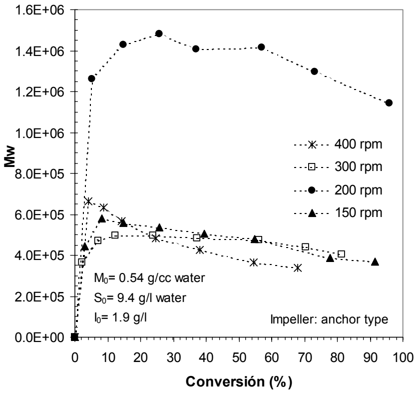

Figure 4. Effect of stirring speed on the weight average molecular weight (*Mw*) as function of monomer conversion for the conditions of Figure 1.

Nomura et al. [1] obtained similar results at 50ºC; however, an interesting difference between the present work and the one of Nomura et al. is that these latter observed a less pronoun effect of SS on the kinetics. The SS range in which such an effect is not observed is higher and wider in their system (400-600 rpm) than in our system (around 200 rpm). This is, shear-induced (orthokinetic) coagulation seems to be more marked in the present work.

The weight average molecular weight (*Mw*) results shown in Figure 4 are consistent with this statement. It can be observed in this figure that the *Mw* obtained at 200 rpm is one order of magnitude higher than in the other runs. In contrast, in Nomura's work the value of *M* obtained at 800 rpm becomes slightly smaller than the one obtained at 410 rpm only after a monomer conversion of ~0.6. It has been pointed out [3] that limited coagulation of polymer latex particles leads to a decrease in *M* when the rate of coagulation is faster than the rate of chain transfer to monomer. The argument is that the radicals contained in the parent particles undergo bimolecular termination when they coalesce to form a single particle, process called [3] coagulative termination. Therefore, because coagulative entry in the Nomura et al. experiments was not as extensive as in the present work, they obtained a less marked effect of SS on *M*.

A reduction in *N* leads by itself to a decrease of *M* because the rate of capture per particle (ρ') of oligomeric radicals dissolved in the aqueous phase increases. However, calculations shown in a previous work of the authors [3], indicates that ρ' would have to increase at least one order of magnitude and become comparable to the rate of chain transfer to monomer to have a significant effect on *M*. Variation of *N* and *Mw* at different SS relative to the respective values obtained at 200 rpm are shown in Table I. It can be observed that the variation of *M* at 300 and 400 rpm is significantly greater than the variation of *N*, suggesting that coagulative termination is playing an important role.

It is also interesting to notice in Figure 4 that the *Mw* values obtained at 150 rpm were as low as those in the runs performed at 300 and 400 rpm. Of course, in the former case such a low *Mw* values were due to monomer transport limitations whereas in the other cases were due to coagulative entry.

Table 1. Variation of the number of particles (*N*) and weight average molecular weight (*Mw*) at different stirring speeds relatives to the values obtained at 200 rpm.

RPM	Final *N* [a]	Var. *N* (%)	Final *Mw*	Var. *Mw* (%)
400	6.6×10^{14}	-44	3.39×10^{5}	70
300	8.3×10^{14}	-30	4.06×10^{5}	64
200	1.19×10^{15}	0	1.143×10^{6}	0

[a] particles/cc water.

The fact that there are significant differences between the results of Nomura et al., and the present one, concerning the optimum SS range (i.e. when the agitation effects are minimized), have important implications. Most of the kinetic studies reported in the literature implicitly or explicitly disregard this effect; therefore, it is questionable if such studies were performed under comparable conditions. Caution should be taken to extent the conclusions obtained in a given system to another one if there is not information available of the optimum SS range for the systems under consideration.

Conclusions

In the present work, the kinetics of styrene emulsion polymerization at 70ºC, using SDS as surfactant and KPS as initiator was studied. From the differences between Nomura et al. [1] results and the ones obtained in the present work it is deduced that the optimum SS range strongly depends on the hydrodynamic characteristics of the reactor and the polymerization conditions. Above the optimum SS range, polymer latex particles tends to undergo limited coagulation leading to a decrease in *Mw* caused by the increment of the free-radical entry frequency. These radicals come from the aqueous phase (oligomeric radicals) and from the radicals contained in the particles subject of coagulation (coagulative entry).

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