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Diffusional Limitations in Emulsion Polymerization

M. Zubitur, J. Mendoza, J.C. de la Cal, J.M. Asua*

Institute for Polymer Materials POLYMAT and Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo 1072, 20080 San Sebastián, Spain.
* Email: qppasgoj@sq.ehu.es

SUMMARY: The effect of diffusional limitations on the kinetics of the process and the molecular weights of the polymer produced by both batch and semicontinuous emulsion polymerization was investigated. A mathematical model that accounts for the main effects observed experimentally was developed

Introduction

Emulsion polymerization is a multiphase system that includes polymer particles, aqueous phase and monomer droplets. In order to reach the polymerization loci, the monomer should diffuse from the droplets to the aqueous phase, through the aqueous phase and from the aqueous phase to the polymer particles. In most academic studies it is considered that the characteristic time for monomer diffusion is much shorter than that of the polymerization, and hence that the rate-determining step is the polymerization reaction. This also implies that the monomer partitioning is ruled by the thermodynamic equilibrium. However, there are indications that, in some occasions, monomer mass transfer may be slower than polymerization. Thus, in the emulsion polymerization of vinyl acetate and veova 10 monitored by calorimetry, Sáenz de Buruaga et al. (Ref.1) found a 2 min delay between the oscillations of the amount of monomer in the reactor and the oscillations of the heat generation rate. This was attributed to monomer mass transfer limitations. Similar results were obtained in the emulsion terpolymerization of methyl methacrylate, styrene and butyl acrylate (Ref.2) Furthermore, there is considerable evidence that chain transfer agents are also subjected to mass transfer limitations (Refs.3-4). This has a critical effect on the feasibility of an effective control of the molecular weight distribution of the polymer.

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In this work an extensive study on the effect of the diffusional limitations on emulsion polymerization was carried out. Both batch and semicontinuous reactors were considered and several monomer systems were investigated.

Batch Emulsion Polymerizations

The effect of the CTA (dodecyl mercaptan) mass transfer on the kinetics of the emulsion polymerization of styrene was investigated. Preliminary calculations showed that the rate-controlling step for mass transfer is likely the CTA mass transfer from monomer droplets to aqueous phase. This process depends on the interfacial area, mass transfer coefficient and equilibrium coefficients across the interface. The experimental design attempted to modify these characteristics. Thus, the effect of the amount of emulsifier, droplet nucleation, agitation, and pH on the kinetics and MWDs was investigated.

The amount of emulsifier was varied in an attempt to modify the size of the monomer droplets and hence the droplet-water interfacial area. Figure 1 shows that an increase of emulsifier concentration led to a reduction of the molecular weights, presumably due to an increase of the CTA concentration in the polymer particles. This effect cannot be due to the increase of the number of polymer particles and decrease of $\bar{n}$ observed as the emulsifier concentration increased, because these factors yield an increase of $\overline{M}_w$.

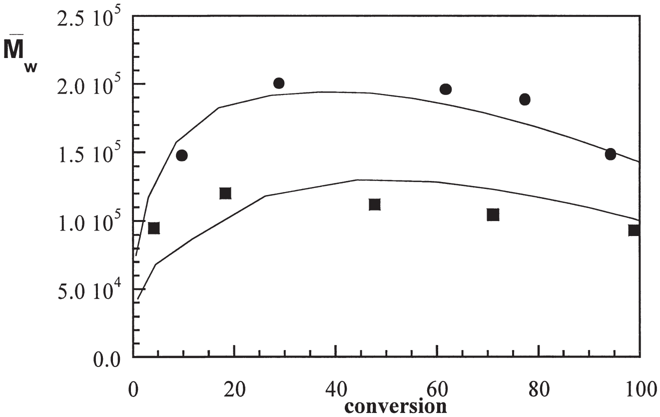

Figure 1.- Effect of the emulsifier concentration on the weight average molecular weight. Legend: (●) 1% based on monomer; (■) 2% based on monomers.

A way to reduce the mass transfer limitations is to nucleate the monomer droplets were the CTA is dissolved. This may be achieved using miniemulsion polymerization (Ref 5). It is worth pointing out that $\bar{n}$ for the conventional emulsion polymerization was slightly lower than that of the miniemulsion process, which in the absence of CTA would also give higher molecular weights for the conventional emulsion polymerization. However, the increase would be much lower than the order of magnitude observed. Three reactions were carried out: run 1 was a conventional emulsion polymerization using 1 wt % of dodecyl mercaptan; run 2 was a miniemulsion polymerization carried out using 1 wt% of dodecyl mercaptan and 1 wt% of hexadecane (to avoid the Ostwald ripening effect); and run 3 was a miniemulsion polymerization using the same recipe as in run 2 but no CTA. Figure 2 compares the molecular weights of the final latex obtained in these polymerizations. It can be seen that the highest molecular weight was obtained in run 3 where no CTA was used. On the other hand, the molecular weights in run 2 were significantly lower than those obtained in run 1. This clearly shows that in conventional emulsion polymerization (run 1) the mass transfer of CTA was diffusionally controlled. Furthermore, it was found that the CTA had no effect on the miniemulsion polymerization rate.

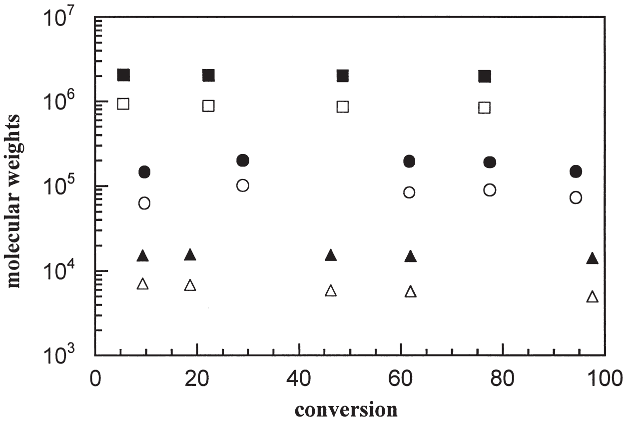

Figure 2.- Effect of droplet nucleation on Mw. Legend: Miniemulsion with CTA (△ Mn, ▲ Mw); conventional emulsion with CTA (○ Mn, ● Mw); miniemulsion witout CTA (□ Mn, ■ Mw).

Agitation affects both the total interfacial area (by reducing the droplet size) and the mass transfer coefficient (by affecting the hydrodynamics around the monomer droplet). Polymerizations at different agitation rates using a 4-paddle stirrer were carried out. The lowest paddle was an anchor and the other three were 45° pitched paddles arranged in such a way that each paddle was perpendicular to the adjacent ones. Agitation rate had no effect on the polymerization rate, i.e., it had no effect on the monomer transport. On the other hand, Figure 3 shows that the molecular weights decreased as the agitation rate increased. Mathematical modelling shows that the improvement of the CTA mass transfer was mainly due to a better emulsification of the monomer droplets .

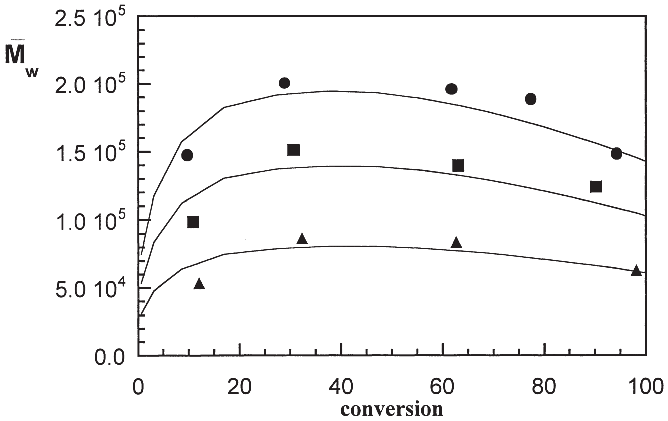

Figure 3 .- Effect of the agitation rate on Mw. Legend: (●) 200 rpm; (■) 275 rpm; (▲) 350 rpm.

Mercaptans are weak acids that can be ionized at high pH. This will increase the solubility of the CTA in water improving its mass transfer. Figure 4 presents the effect of the pH on the molecular weights. It can be seen that the higher the pH the lower the molecular weight. Surprisingly, no significant effect of the pH on the kinetics was observed, i.e., desorption of CTA radicals was not substantial.

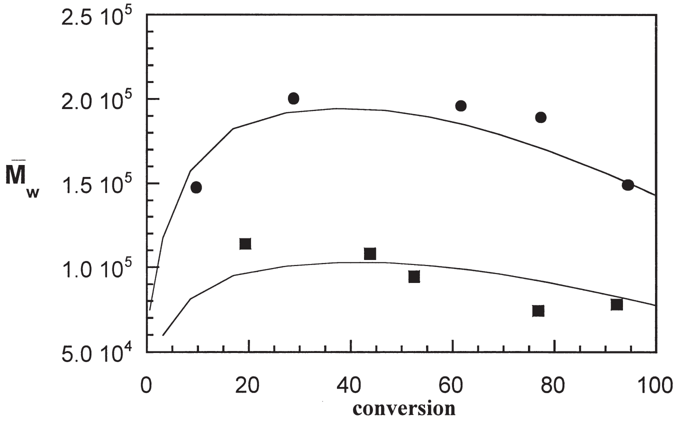

Figure 4.- Effect of pH on Mw. Legend: (●) pH = 8;(■) pH = 12.

Mathematical Model

A mathematical model for the process was developed. The model considers micellar nucleation, partitioning of the monomer according to the thermodynamic equilibrium, and diffusionally limited CTA mass transfer, the droplet-water mass transfer being the rate determining step. The outputs of the model are monomer and CTA conversion, number of polymer particles, and molecular weights of the polymer. Figures 1, 3 and 4 present a comparison between the experimental results and the model predictions. It can be seen that a fairly good agreement was achieved.

Semicontinuous Emulsion Polymerizations

Most emulsion polymerizations are carried out in semicontinuous reactors because this process allows a good control of both the properties of the latex and the reactor temperature. In such a process, monomers, and sometimes, initiators, emulsifiers, chain transfer agents (CTA) and water are fed into the reactor during the operation. Monomers may be fed neat or pre-emulsified. The effect of both the agitation and pre-emulsification on the kinetics and MWDs was investigated for the emulsion copolymerization of styrene and butyl acrylate. An anchor stirrer was used in these experiments. In order to differentiate monomer mass transfer from CTA mass transfer, experiments with and without CTA (dodecyl mercaptan) in the formulation were carried out.

Figures 5 and 6 show the effect of the agitation rate on the instantaneous conversion and MWDs, respectively, in 34 wt% solids content polymerizations carried out feeding neat monomers and no CTA. It can be seen that agitation affected markedly monomer conversion at low rpm, but conversion was independent of agitation at high rpm. It has to be pointed out that some monomer pooling was observed at 70 and 100 rpm. Figure 5 shows that the process was diffusionally controlled at 70 and 100 rpm, quite likely due to the poor emulsification of the entering monomer, which resulted in a low monomer-water interfacial area. At agitation rates higher than 150 rpm, the agitation was strong enough to emulsify the monomer and the process became kinetically controlled. On the other hand, Figure 6 shows that the molecular weights increased with agitation rate at low rpm and were almost constant at high agitation rates. These results are also consistent with a diffusional control of the monomer mass transfer at low rpms.

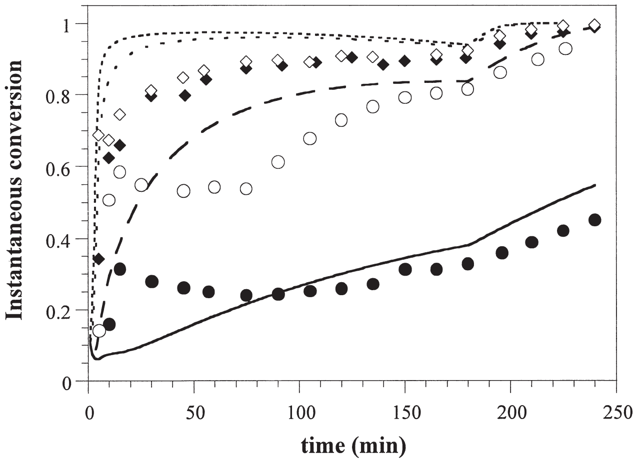

Figure 5.- Time evolution of the instantaneous conversion of the reactions carried out feeding neat monomers (without CTA and 34 wt% solids content, monomers St/BuA). Points (experimental results): (●) N=70 rpm, ( ) N=100 rpm, (◆) N=150 rpm, ( ) N=220 rpm, Lines (model simulations): (—) N=70 rpm, (– –) N=100 rpm, (. . .) N=150 rpm, (---) N=220 rpm.

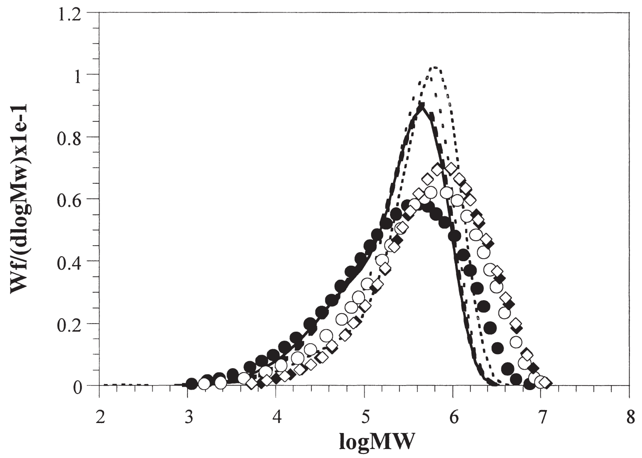

Figure 6.- Molecular weight distribution of the final latex of the reactions carried out feeding neat monomers (without CTA and 34 wt% solids content, monomers St/BuA). Points (experimental results): (●) N=70 rpm, ( ) N=100 rpm, (◆) N=150 rpm, ( ) N=220 rpm, Lines (model simulations): (—) N=70 rpm, (– –) N=100 rpm, (. . .) N=150 rpm, (---) N=220 rpm.

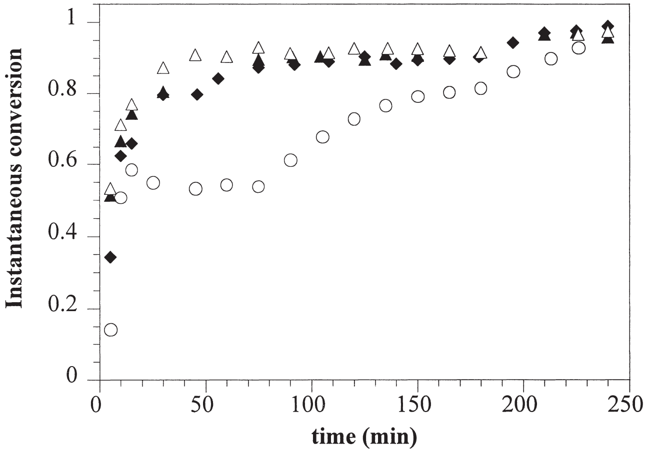

Figure 7.- Time evolution of the instantaneous conversion of the reactions carried out feeding neat monomers or preemulsion (without CTA and 34 wt% solids content, monomers St/BuA): ( ) N=100 rpm neat monomers, (◆) N=150 rpm neat monomers, (▲) N=100 rpm preemulsion, ( ) N=150 rpm preemulsion.

The agitation was less critical if the monomers were fed as a pre-emulsion. In that case no effect of the agitation rate on both kinetics, (Figure 7) and MWDs, (not shown) was found for agitation rates over 100 rpm. These results show that the small pre-emulsified monomer droplets presented an interfacial area large enough to ensure an efficient mass transfer. When CTA was included in the formulation, the evolution of the monomer conversion in the polymerizations carried out feeding neat monomer was similar to that shown in Figure 5. However, the molecular weights decreased as agitation rate increased because the increase in CTA concentration in the polymer particles overcame the effect of the increase in monomer concentration (Figure 8).

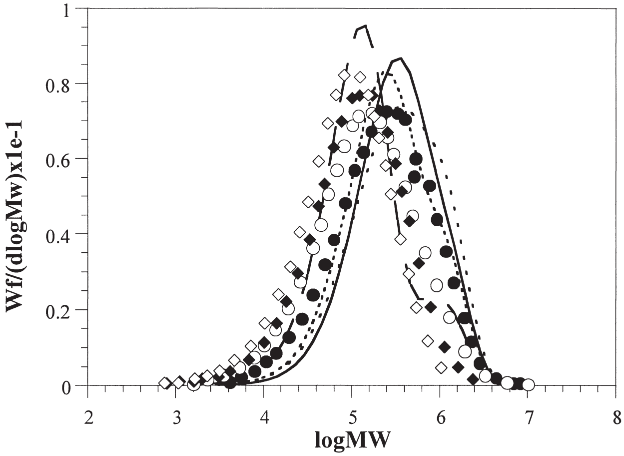

Figure 8.- MWD of the final latex of the reactions carried out feeding neat monomers (with CTA and 34 wt% solids content, monomers St/BuA). Points (experimental results): (●) N=70 rpm, ( ) N=100 rpm, (◆) N=150 rpm, ( ) N=220 rpm, Lines (model simulations): (....) N=70 rpm, (—) N=100 rpm, (---) N=150 rpm, (- –) N=220 rpm.

No diffusional limitations were found for agitation rates equal or greater than 100 rpm in the emulsion copolymerization of St and BuA carried out at high solids content (55 wt %) and using neat monomer addition. However, in the polymerization carried out at 70 rpm some monomer pooling was observed and the polymerization could not be completed because massive coagulation occurred.

The effect of the water solubility of the monomer system was investigated by changing the styrene by a more water-soluble monomer as vinyl acetate. It was found that in the range of agitation rates used (70-220 rpm), the kinetics was independent of the agitation rate, namely, the process was kinetically controlled. This means that the agitation requirements are much more exigent for water-insoluble monomers. Figure 9 presents the effect of agitation on the particle size distribution measured by disc centrifuge. It can be seen that particle size increases with agitation rate quite likely due to limited coagulation. Figure 10 shows that the MWDs were independent of agitation rate when dodecyl mercaptan was included in the formulation (55 wt% solids, neat monomer feed). This is somehow surprising as this CTA is rather water-insoluble. It is a matter of speculation if this was due to the presence of water-soluble monomers which may change the character of the aqueous phase increasing the solubility of the CTA or to the high solids formulation which increments the mass transfer by collision.

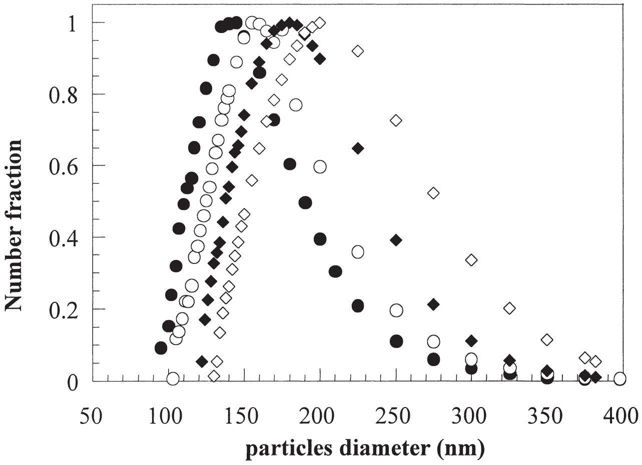

Figure 9.- Particle size distribution of the reactions carried out feeding neat monomers (without CTA and 55 wt% solids content, monomers Vac/BuA): (●) N=70 rpm, (○) N=100 rpm, (◆) N=150 rpm, ( ) N=220 rpm.

Mathematical Model

A mathematical model for the process was developed. The model accounts for the emulsification process (when neat monomer is fed into the reactor), monomer and CTA mass transfer from the droplets to the aqueous phase, through the aqueous phase and form the aqueous phase to the polymer particles, as well as for the polymerization in the polymer particles. Figure 5 presents a comparison between the experimental results and model predictions for the evolution of the monomer conversion. It can be seen that the model predicted well the effect of the agitation rate on the kinetics. The model was also able to predict the increase of molecular weight in reactions without CTA (Figure 6), as well as the decrease of the molecular weight in reactions with CTA (Figure 8) when the agitation rate was increased.

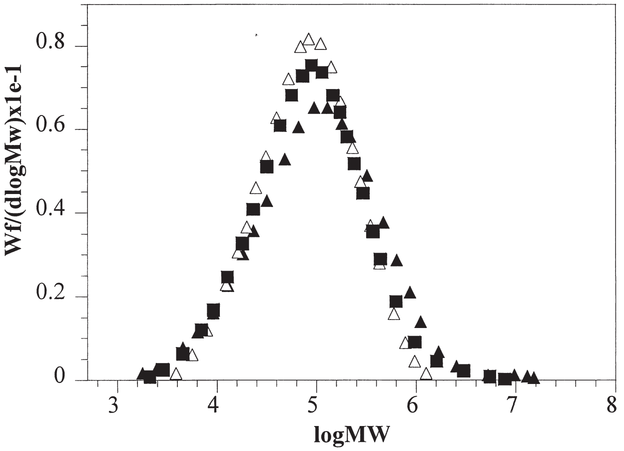

Figure 10.- Molecular weight distribution of the final latex of the reactions carried out feeding neat monomers (with CTA and 55 wt% solids content, monomers VAc/BuA): (▲) N=70 rpm, (△) N=150 rpm, (■) N=220 rpm.

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