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The emulsion polymerization of styrene, activated by microwave irradiation and conductive heating, was modeled using the Predici® simulation package of CiT. Microwave activated initiation was modeled as adding a second conventional free-radical chemical initiator, whose concentration is given by the intensity of microwave irradiation, and its "decomposition" kinetic rate constant is related to the ratio of monomer concentration to the rate of absorbed radiation. Most of the kinetic rate constants and model parameters used in the model were taken from the literature, in order to avoid unnecessary parameter estimation procedures. Model predictions of conversion, number and weight average molecular weights, for microwave and thermally activated systems, agree well with the experimental data reported in the literature, including experimental data previously reported by our own group.

Keywords microwave emulsion polymerization, modeling, polystyrene, Predici®

Introduction

The emulsion polymerization of styrene has been studied widely (1, 2). Different types of chemical and physical activation methods have been reported. Visible light, UV, short wave and high frequency radiation have produced good quality polystyrene.

The use of microwave irradiation as a source of energy, to activate chemical reactions, is indicating more relevance lately, due to their appealing advantages over conventional thermal activation methods. Microwave irradiation has proved to be a rapid method of activation for polymerization reactions, and the process also results in considerable savings of energy, compared to traditional conductive heating. Several studies on the microwave irradiated emulsion polymerization of styrene (3–5) and methyl methacrylate

(6, 7) have been reported, and a recent review on microwave assisted polymer synthesis is available (8).

The modeling of emulsion polymerization with thermal activation has been addressed significantly in the literature (1, 2, 9, 10). Madras and Karmore (11) developed a mathematical model for simultaneous polymer addition and degradation of poly(methyl methacrylate) with microwave radiation, and compared their model predictions against experimental data. They suggested that although the reaction rates are significantly enhanced in the presence of microwaves, the reaction mechanism is unaffected. They reported good agreement between model predictions and experimental data, for molecular weight development.

Palacios and Valverde (3), Correa et al. (4) and Zhu et al. (5) have used microwave irradiation in combination with $K_2S_2O_8$, potassium persulphate (KPS), to activate the emulsion polymerization of styrene. In this paper, the emulsion polymerization of styrene, activated by microwave irradiation and conductive heating at the experimental conditions described in the above mentioned studies was modeled using the simulation package Predici®, developed by M. Wulkow of CiT, Germany.

Model Building

Details on the Studied Formulation and Process Conditions. The system studied in this work is the microwave activated (MA) emulsion polymerization of styrene, at the same conditions described in Table 1.

Table 1
Recipe and process conditions for the MA emulsion polymerization of styrene

Component or variable	Amount or value (Units)			
	Palacios and Valverde (3)	Zhu et al. (5)	Correa et al. (4)	
Water	300 g	30 g	30 g	30 g
SDS (surfactant) Sodium dodecil sulphate	1.266 g	0.3 g	1.24 wt%	1.24 wt%
KPS (initiator) Potassium persulphate	1.92 mol L^{-1}	0.2 wt%	0.04 wt%	0.12 wt%
Styrene monomer	21.7 g	8.594 g	8.594 g	8.594 g
Polystyrene seed	0.22 g $M_n = 289 \times 10^{-5}$ g mol^{-1}; PDI = 2.1			
Temperature	50°C	70°C	70°C	70°C
Microwave power	389 W	120 kW	800 W	175 W 800 W
Supplied energy	389 J s^{-1}	120 kJ s^{-1}	800 J s^{-1}	175 J s^{-1} 800 J s^{-1}
Absorbed energy	24.31 J s^{-1}	54 kJ s^{-1}	36 J s^{-1}	7.88 J s^{-1}
Irradiation time	33 min	90 min	6 min	6 min

Reaction Mechanism

The reaction mechanism for the microwave emulsion polymerization of styrene is, in essence, the same one as in a conventional free-radical emulsion polymerization, namely: initiation, propagation, chain transfer and termination reactions, coupled to a phase equilibrium problem, to calculate the distribution of components among the phases. In order to model the dispersed phase polymerization in Predici®, the following phase transition steps were needed: monomer precipitation, equilibrium between the aqueous and polymer (latex) phases, and oligomer transfer from the aqueous to the latex phase. The reactions included in the model are summarized in Table 2. The reason why a critical length of 3 monomer units is used to assume transfer of oligomers from the aqueous to the latex phase (see the propagation reactions in the aqueous phase in Table 2) is explained in the following section of this paper. The transfer and equilibrium steps used to take into account the transfer of species among phases are listed in Table 3. The approach used for modeling of emulsion polymerization with the Predici® simulation package of CiT will be briefly explained later in this paper.

The only difference from a conventional emulsion polymerization in the modeling of microwave activated seeded emulsion polymerization used in this paper is that the initiator concentration is considered to be the intensity of the microwave irradiation, and the proper definition of the initiator decomposition kinetic rate constant and efficiency, as explained in the following section.

Modeling Considerations

The generation of free radicals in microwave activated emulsion polymerization of styrene basically comes from two sources: chemical initiation with the initiator (KPS), and activation from microwave irradiation. Therefore, the total rate of radical generation is given by the rate of radicals generated from chemical initiation plus the rate of radicals activated by microwave irradiation. The rate of radical generation from radiation activation, $r_{I,mv}$, is given by Equation (1), where k_i is a kinetic rate constant, which is

Table 2
Reaction mechanism

Name	Reaction
Chemical initiation (KPS)	$I \xrightarrow{k_d} 2I^\bullet$
Microwave promoted initiation	$M_{aq}(\text{"Radi"}) \xrightarrow{k_{ir}} 2R_1^\bullet$
Propagation in the aqueous phase	$I^\bullet + M_{aq} \xrightarrow{k_{p1}} R_1^\bullet$
	$R_1^\bullet + M_{aq} \xrightarrow{k_{p2}} R_2^\bullet$
	$R_2^\bullet + M_{aq} \xrightarrow{k_{p3}} R_3^\bullet$
Initiation in the particle (latex) phase	$I_p^\bullet \xrightarrow{k_{fast}} R_1^\bullet$ (see Table 3 for formation of $I_p^\bullet$)
Propagation	$R_r^\bullet + M_p \xrightarrow{k_p} R_{r+1}^\bullet$
Transfer to monomer	$R_r^\bullet + M_p \xrightarrow{k_{fm}} R_1^\bullet + P_r$
Termination by combination	$R_r^\bullet + R_s^\bullet \xrightarrow{k_{tc}} P_{r+s}$

Table 3
Transfer and equilibrium steps

Name	Step
Monomer precipitation	$M_{aq} \xrightarrow{k_{pre}} M_{pre}$
Equilibrium	$M_{aq} \xleftrightarrow{K_{eq}} M_p$
Phase transfer	$R_3^\bullet \xrightarrow{k_{pht}} I_p^\bullet$

defined in Equation (2), (2).

$$r_{I,mv} = k_i r_{mv} \tag{1}$$

$$k_i = \frac{[M]}{r_{mv} t} \tag{2}$$

[M] in Equation (2) is the monomer concentration, and r_{mv} is the rate of absorbed microwave irradiation, given in terms of the radiation dose, and t is the irradiation time.

The microwave initiation efficiency, f_r, was taken as the ratio of absorbed to supplied energies, as shown in Equation (3).

$$f_r = \frac{E_{abs}}{E_{sup}} \tag{3}$$

The transfer of polymer radicals from the continuous (aqueous) phase to the particle (latex) phase is modeled according to the mechanism proposed by Gilbert (13). The rate-determining step is the growth of polymer radicals in the aqueous phase, to a critical degree of polymerization, z, which renders the polymer radicals surface active. Surface active radicals are then assumed to irreversibly enter the monomer droplets, without further reacting in the aqueous phase. The value of z for KPS-derived radicals is given by Equation (4), (13).

$$z = 1 + \frac{-23\,\text{kJ mol}^{-1}}{RT \ln Cw^{sat}} \tag{4}$$

Cw^{sat} in Equation (4) is the solubility of the surface-active radicals in the aqueous phase at temperature T, and R is the ideal gas constant. At 50°C and $Cw^{sat} = 4.13 \times 10^{-3}$ mol L^{-1}, the critical degree of polymerization, z, turns out to be equal to 3. That is why three propagation steps in the aqueous phase are considered in the reaction mechanism of Table 2.

The kinetic rate constants and model parameters used in our model are summarized in Table 4. It is worth mentioning that all these values were gathered from the literature, and only the kinetic constant for "monomer precipitation" was needed to be fine-tuned, in order to reproduce all the experimental data available.

In order to preserve phase equilibrium, the chemical species that are soluble in both, styrene and water, will partition among the aqueous and organic (droplet and latex) phases. Modeling studies indicate that the rate of interfacial mass transfer is sufficiently fast under typical polymerization conditions, such that phase equilibrium can be assumed at all times for low molecular weight chemical species, i.e., styrene monomer and styrene oligomeric radicals (14).

Table 4
Kinetic rate constants and other model parameters

Coefficients	Value/Expression		References
	50°C	70°C	
C_p	$5.5 \, \text{mol L}^{-1}$	$5.8 \, \text{mol L}^{-1}$	Gilbert (13)
C_w	$4.13 \times 10^{-3} \, \text{mol L}^{-1}$	$5.6 \times 10^{-3} \, \text{mol L}^{-1}$	Gilbert (13)
f	0.5	0.5	Gao and Penlidis (2)
f_r	0.0625	0.045	Aguilar and Almanza (15)
K_{eq}	1400	1400	Gao and Penlidis (2)
k_d	$6 \times 10^{-5} \, \text{min}^{-1}$	$9.12 \times 10^{-4} \, \text{min}^{-1}$	Gao and Penlidis (2)
k_{fast}	$6 \times 10^4 \, \text{L mol}^{-1} \text{min}^{-1}$	$1.1624 \times 10^6 \, \text{L mol}^{-1} \text{min}^{-1}$	Gilbert (13)
k_{ir}	5.3184×10^{-7}	9.0334×10^{-7}	Ivanov (12)
k_p	$1.5 \times 10^4 \, \text{L mol}^{-1} \text{min}^{-1}$	$2.88 \times 10^4 \, \text{L mol}^{-1} \text{min}^{-1}$	Buback et al. (16)
k_{p1}	$4 \, k_p$	$4 \, k_p$	Deady et al. (17)
k_{p2}	$3 \, k_p$	$3 \, k_p$	Deady et al. (17)
k_{p3}	$2 \, k_p$	$2 \, k_p$	Deady et al. (17)
k_{pht}	$3.8685 \times 10^{12} \, \text{L mol}^{-1} \text{min}^{-1}$	$4.6215 \times 10^{16} \, \text{L mol}^{-1} \text{min}^{-1}$	Gilbert (13)
k_{pre}	$5 \times 10^3 \, \text{min}^{-1}$	$5 \, \text{min}^{-1}$	Guessed
k_{tc}	$1.0569 \times 10^8 \, \text{L mol}^{-1} \text{min}^{-1}$	$1.3824 \times 10^8 \, \text{L mol}^{-1} \text{min}^{-1}$	Gao and Penlidis (2)
k_{fm}	$5.668 \times 10^{-1} \, \text{L mol}^{-1} \text{min}^{-1}$	$9.9611 \, \text{L mol}^{-1} \text{min}^{-1}$	Gao and Penlidis (2)

Modeling of Emulsion Polymerization in Predici® (18)

Predici® provides a framework for the treatment of heterogeneous systems, such as emulsion polymerization, in which particles exist in different phases of a reactor, but may also switch their phases by phase transfer. This framework consists of: (1) two additional phases in a reactor (often called *second* and *third* phases, the third reactive phase being a special feature of Predici®, not described here explicitly, since its structure and treatment are the same as for the second phase) containing arbitrary reactants and reactions, (2) the possibility to declare a low molecular weight reactant to be in its own phase, without reactions, and (3) transition steps between the phases.

The implementation of the system studied in this paper is a modification of example phase1.rsy of the Predici® simulation package, which is a model for an emulsion homopolymerization with a certain monomer split into three components: M_{aq} (in water phase), M_p (in polymer phase), M_{pre} (precipitated in droplets). The radical polymerization is started in the water phase and goes up to chains with 3 monomer units, as calculated from Equation (4). The radical chains of this critical size enter the second phase immediately, by forming a new particle (by use of step *Phase transfer*). The number of particles is balanced by a library variable of the type *Equation*, and a related interpreter file. In the polymer phase, radical chains are initialized and a standard radical polymerization scheme is modeled. The solubilities of the monomer in the water phase (cw_m), and in the polymer phase (cp_m), control the flow between the phases. The precipitation and formation of droplets is modeled by using the step *Precipitation*. The exchange of monomer between water and polymer phase is performed by the step *Equilibrium*.

One important modification to the above description is that the effect of microwave irradiation was modeled in Predici® as having a second initiator in the formulation. Figure 1 shows the Workshop "Modules" window of Predici®, where the steps used to model the microwave irradiated emulsion polymerization of styrene are displayed. The dummy initiator is shown as "Radi", in the fourth step of the Predici® "Modules" window, shown in Figure 1.

Results and Discussion

As mentioned before, Predici® was used to model the emulsion polymerization of styrene, activated by conductive heating in the presence of KPS as initiator, as well as the case of combined activation with microwave irradiation and chemical initiation from conductive heating. Model predictions of conversion, and number and weight average molecular weights were compared against the experimental data available in the literature for this type of system (3–5), in order to assess the performance of the model.

In order to test the performance of Predici® to model emulsion polymerization systems with no irradiation, some of the conditions studied by Harada et al. (19) and Salazar et al. (20) for emulsion polymerization of styrene at 50 and 70°C, respectively, were simulated. Figure 2 shows a comparison of predicted profiles obtained with Predici® (solid lines) against the experimental data of Harada et al., at 50°C and two different emulsifier concentrations. The way to supply the emulsifier concentration to Predici® was through the number of particles at that concentration, which was known (19). Most of the kinetic and model parameters were given values from the literature. The only parameter that was tuned to fit the experimental data was the kinetic constant for monomer precipitation, k_{pre}. As observed, the predicted polymerization rate is somewhat higher than the experimental data at low conversion, particularly for the high
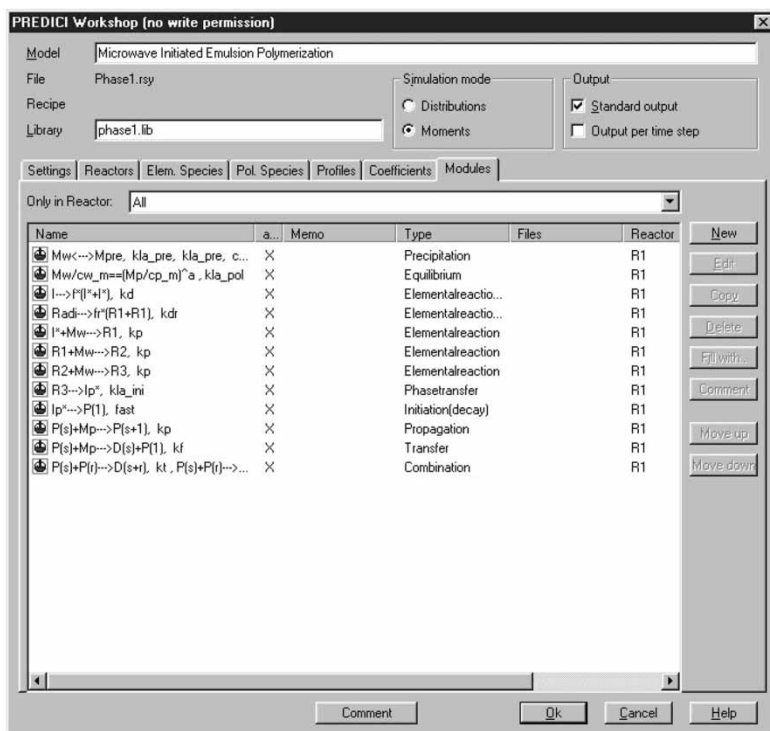
Figure 1. Modules of Predici® used to model microwave irradiated emulsion polymerization.
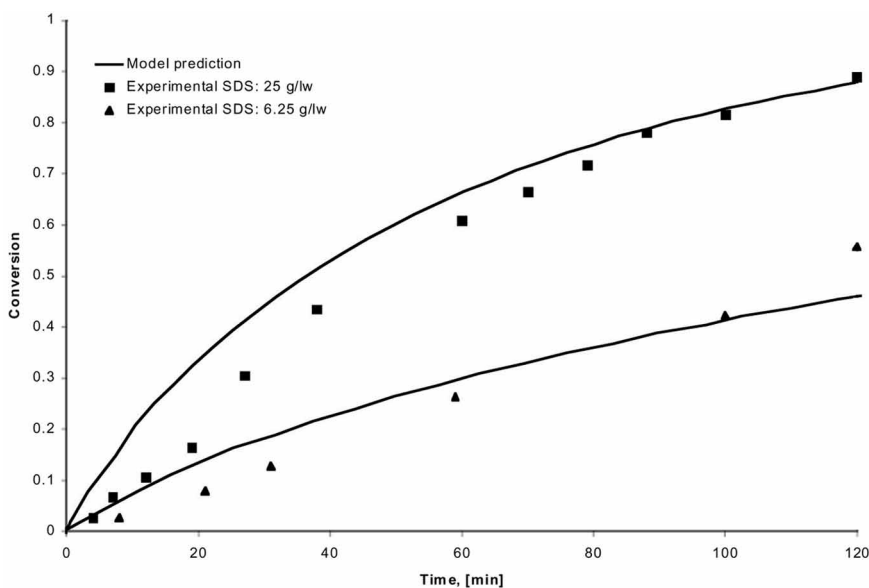

Figure 2. Simulation of the effect of emulsifier on the emulsion polymerization of styrene at 50°C (solid lines). Water: 1 L, monomer: 572 mL, [KPS] = 0.0046 mol/L of water, [SDS] = 6.25 (▲), 25 (■) g/L of water. Experimental data from Harada et al. (19).

emulsifier concentration case, but the agreement is very good at intermediate and high conversions. Gao and Penlidis (2) also modeled this system using Emulpoly, a powerful simulation package designed specifically for emulsion polymerization systems. Our simulations at the low emulsifier concentration seem to be better than those obtained by Gao and Penlidis (2), and our simulations at the high emulsifier concentration show more deviation than theirs at the low conversion range. Figure 3 shows the corresponding comparison at 70°C, using the experimental data of Salazar et al. (20). It is observed that the agreement is better than at 50°C. It turns out that the agreement between experimental data and model predictions obtained with Emulpoly is also better at 70°C (2). Since the kinetic rate constants used were basically the same, the small differences between the two simulation packages should come from the models for partition of species among the phases, namely, on the phase equilibria model equations.

In Figure 4, the predicted profiles of monomer conversion versus time, for the two conductive heating (CH) and microwave activated (MA or MW in the figure), are compared against our own experimental data (3). It is observed that the agreement between the predicted profile and the experimental data, for the case of combined chemical and microwave promoted initiation (MA) is fairly good, at low and intermediate conversions. In the high conversion region, the model seems to overestimate the rate of polymerization, shown as higher than experimental conversions. In the case of conductive heating (CH), i.e., chemical initiation without microwave irradiation, the overall agreement between experimental data and predicted model profiles is good, but it is observed that at low and intermediate conversions, up to about 50% monomer conversion, the model predictions overestimate the polymerization conversion, and at high conversions, as in the case of 50% monomer conversion or higher, the model predicted profile lies below the experimental data. This small over prediction should not be caused by any microwave-related effect, since the same trend was observed for the CH system modeled in Figure 2. Once again, it is worth mentioning that the only parameter that
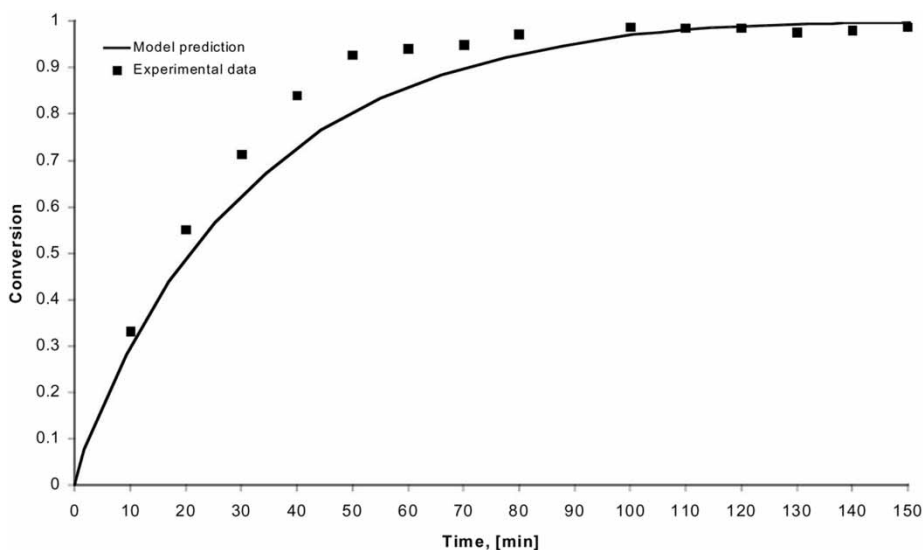

Figure 3. Simulation of styrene emulsion polymerization at 70°C (solid line). Styrene: 130.7 g, water: 515.6 mL, KPS: 0.233 g, SDS: 2.62 g. Experimental data (■) from Salazar et al. (20).
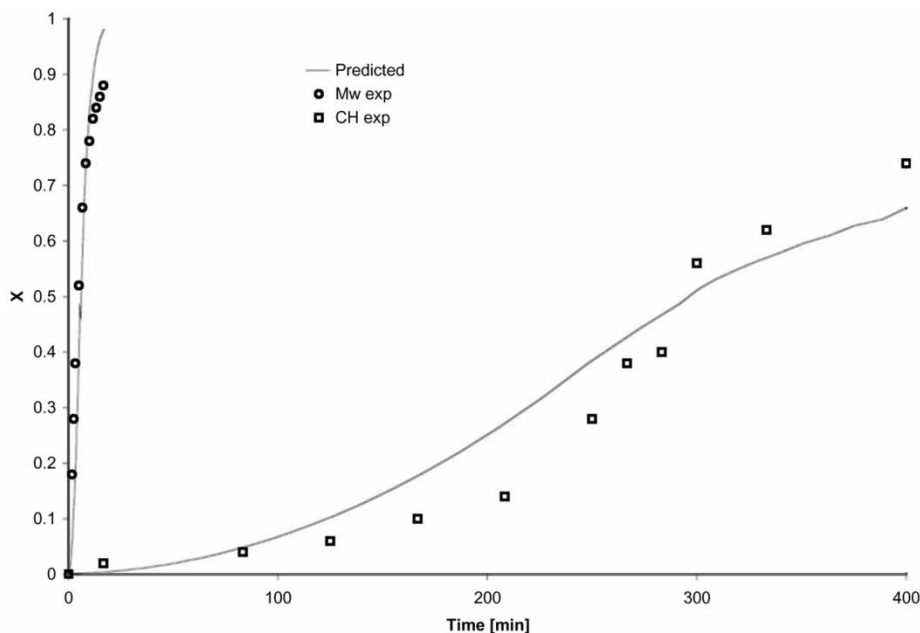
Figure 4. Comparison of predicted conversion versus time profiles against experimental data, in the microwave emulsion polymerization of styrene. Predicted profiles using Predici® (solid lines), conductive heating (□), microwave activation (○).

was fine-tuned, in order to match the experimental data, was the kinetic constant for the "monomer precipitation", in the phase transfer step. In the actual situation, the monomer droplets are dispersed in water from the very beginning, given the low solubility of styrene in water. However, since Predici® approaches phase equilibria problems as being kinetically-driven in nature, it is inherently being assumed that the system starts as a single phase, with the formation of the second phase dictated by the kinetic constant of precipitation, k_{pre}. The high value of k_{pre} indicates that the formation of the monomer phase is very fast and, therefore, the essence of the process is not lost by assuming that the phase equilibria process is kinetically driven.

Process simulators are based on mathematical models, which describe the phenomena under study, and they offer the possibility of predicting the development of such phenomena. However, mathematical models are only an approximation to the actual situation under study. Model predictions cannot be any better than what the assumptions behind the model allow. It has been recognized that emulsion polymerization is a very complex system. Even though the system has been studied extensively, there are still several phenomena, which are not fully understood. Nucleation of particles is an example of that. There is still debate in the literature as to which is the correct mechanism of nucleation, if micellar nucleation, homogeneous nucleation, or both (1, 2). Even if a very sound mathematical model is used, there are several issues that need to be addressed, in order to obtain reliable predictions. Some of these issues concern the kinetic rate constants. The spread of reported values on the kinetic rate constants for even the most common reactions, and the most common monomers, is surprisingly high. Therefore, considering the high complexity of the emulsion polymerization

process, it is expected that predicted profiles obtained with even the best mathematical models available in the literature, can show certain degree of disagreement with reported experimental data.

It is clear from Figure 4, that microwave irradiation activates the propagation of styrene in emulsion polymerization, obtaining high polymerization rates in a very short time, in the conversion range studied, compared to the thermal activation process. For instance, 90% monomer conversion is reached in about 20 min, when microwave irradiation is used, whereas less than 5% monomer conversion is reached in the same time period, when only chemical initiation is present. In this last case, it takes over 400 min, to reach 70% monomer conversion.

For the thermal-chemical activation process (CH), the absolute difference at 125 min between the predicted and experimental conversion values was of 0.04. This difference indicates that the predicted value is 1.6 times higher than the experimental value, which indicates that the actual induction time is longer than the one predicted by the model.

In the case of the microwave activation process (MA), the reverse situation was observed, since at 5 min of reaction time, the predicted monomer conversion was 0.52, compared to a value of 0.41, obtained in our experimental study (3). Now, if the monomer conversion at 10 min is analyzed, i.e., a predicted value of 0.82 compared to only 0.78 for the microwave experiment, the difference between both values is 0.04, which corresponds to a 5.1% difference, which can be considered quite low. That means that model predictions for the microwave activated system seem to agree better with the experimental data in the case of microwave activation than in the case of the thermal-chemical activation process.

Figure 5 shows predicted profiles of the number and weight average molecular weights, M_n and M_w, vs. time, for the case where conducting heating plus a chemical initiator was used. Also shown in Figure 5 are the corresponding experimental data, at the end of the polymerizations, which correspond to the high conversion range (15). These values correspond to conversions higher than 90%. The agreement between the measured value of M_n, and the corresponding value calculated with Predici® is very
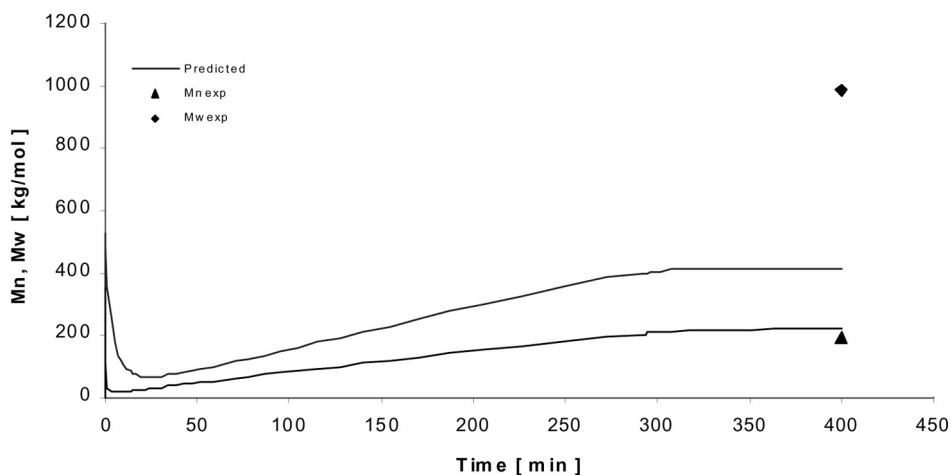

Figure 5. Comparison of predicted M_n and M_w vs. time profiles against experimental data, in the microwave emulsion polymerization of styrene, for conductive heating chemical.

good. However, the measured value of M_w is more than twice the predicted value. It is difficult to establish conclusive arguments as to why such a deviation is observed, with the very limited experimental data available. The differences might be attributed to either experimental error, or to model limitations, such as neglecting diffusion-controlled effects at high conversions. Figure 6 shows a comparison of the predicted profiles of M_n and M_w, versus time, against the experimental data of Aguilar and Almanza (15), for the case of microwave irradiation. In this case, the experimentally measured final values of M_n and M_w agree reasonably well with the simulated profiles. This can be considered an indication that the disagreement observed in Figure 5 might be due to model limitations.

At 8 min of polymerization time, the calculated values of M_n and M_w were 2×10^6 and 4×10^6 g mol^{-1}, respectively. These values are not very different from those of 1.4×10^6 and 3.9×10^6 g mol^{-1}, respectively, obtained by GPC. However, the experimental polydispersity is 1.34 times higher than the calculated value. Figures 5 and 6 show the typical behavior of a microwave initiated emulsion polymerization system, namely, that much faster polymerization rates and much higher molecular weights are obtained, as compared to the simple conductive heating case. Although the calculated absolute values of M_n and M_w are in good agreement with the experimental data (15), the difference in polydispersity is significant. This information is more clearly observed in Table 5.

Although there were not more experimental data available from our group for this monomer, the experimental conditions reported by Zhu et al. (5) and Correa et al. (4) were also modeled, in order to obtain more insight as to the adequacy of Predici® to model microwave activated emulsion polymerization of styrene.

Figure 7 shows a comparison of model predictions against the experimental data of Zhu et al. (5) for both CH and MA cases. It is observed that the agreement is very good for the CH case. In the case of microwave activation, the agreement is very good up to about 0.8 of monomer conversion and 40 min reaction time. From that time on, the experimental data
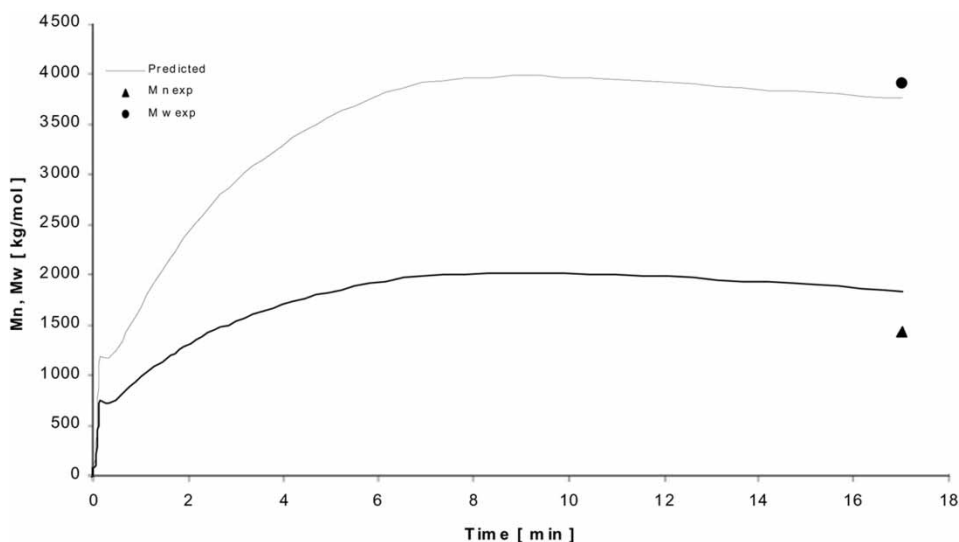

Figure 6. Comparison of predicted M_n and M_w vs. time profiles against experimental data, in the microwave emulsion polymerization of styrene, for microwave irradiation, at 50°C.

Table 5

Predicted and experimental values of number-average molecular weight (M_n) and weight-average molecular weight (M_w) for polystyrene produced by microwave emulsion polymerization

	M_n (kg/mol)	M_w (kg/mol)	PDI
Model	1841.50	3763.69	2.044
Experimental (15)	1434.83	3924.27	2.74

show a conversion limiting behavior at about 0.85 of monomer conversion, whereas the predictions by Predici® indicate that the polymerization proceeds up to total conversion, reached at about 90 min reaction time. That discrepancy could be caused by experimental error, to not considering diffusion-controlled effects (e.g., the glassy effect is characterized by reaching a limiting conversion), or possibly to not having enough initiator to complete the polymerization. Figure 8 shows the corresponding number average molecular weight calculated profiles and experimental data. In the case of conductive heating, the agreement is reasonably good, although the simulated values are slightly over predicted at low conversions, and slightly under predicted at high conversions. In the case of microwave activation, the predicted profile at the very beginning of the polymerization is unrealistically high, decreasing very rapidly to a realistic value, then increasing, and finally decreasing after about 0.7 of monomer conversion. The fast increase and decrease on M_n at the start of
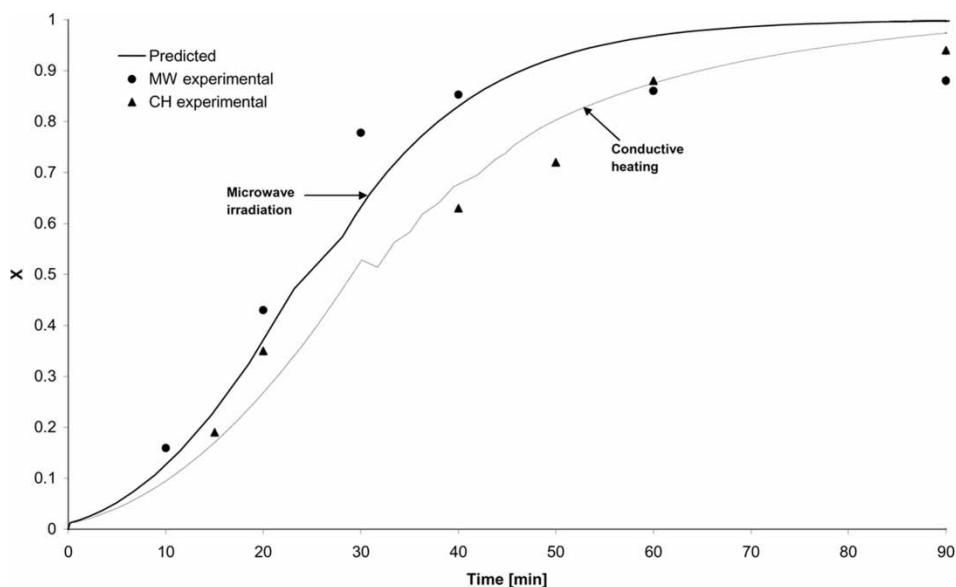

Figure 7. Comparison of conversion versus time profiles for conductive heating (CH) and microwave activation (MA or MW) for emulsion polymerization of styrene. For pulsed microwave irradiation (MA), power: 120 kW, temperature: $71 \pm 2.5°C$, initiator concentration: 0.2 wt%. For CH, temperature: $72 \pm 1°C$ and initiator concentration: 0.2 wt%. Model predictions (solid lines) against experimental data of Zhu et al. (5) for MA (●) and CH (■).
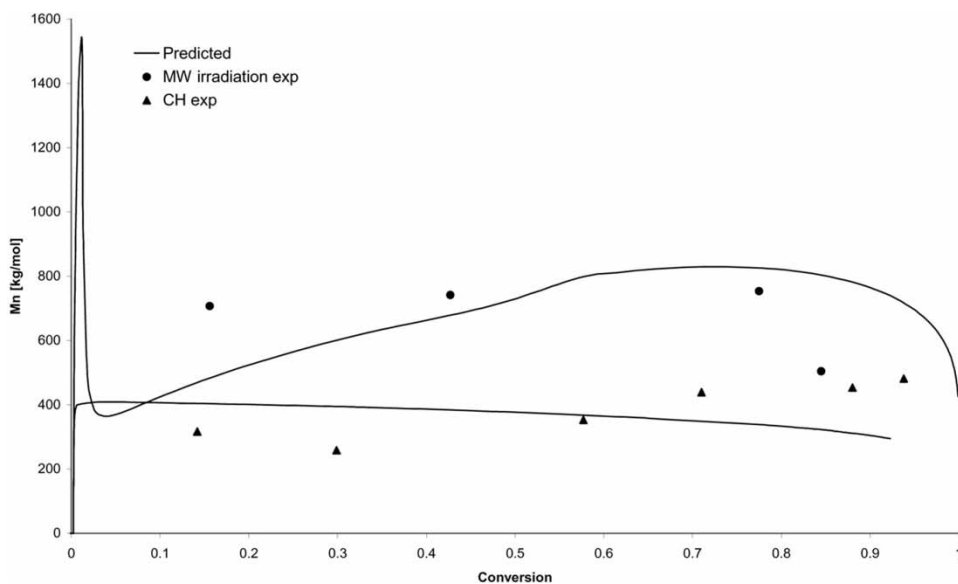
Figure 8. Comparison of predicted profiles of number average molecular weight (M_n) against experimental data of Zhu et al. (5) in emulsion polymerization of styrene with conductive heating (CH) (▲) and microwave activation (MA or MW) (●).

the polymerization could be caused by an inadequate choice of the tolerance required to integrate the system of ordinary differential equations (ODEs) that Predici® internally generates and solves. The simulations were carried out with the default values of all the numerical parameters. In systems with very fast dynamics (as it can be the case with microwave activation), it is convenient to use smaller tolerances (more rigorous criteria for numerical solution of the ODEs). Both the experimental data and the predicted profile for the MA case show a maximum on M_n at about 0.6–0.7 of monomer conversion. The experimental datum at 0.83 monomer conversion seems to show a faster decrease on M_n, but it could well be an outlier point. More experimental data on the high conversion region would be needed to conclude if the shape (decreasing at the end) of the predicted profile is correct or not. A physical cause for a decrease could be the formation of very short polymer molecules at the end of the polymerization. That could happen if propagation is suppressed more meaningfully than termination, and if activation still takes place at high conversions, situations, not unlikely to occur.

Figure 9 shows the predictions and experimental data for polydispersity (DI) versus conversion at the same conditions of Figures 7 and 8. In the case of CH, almost constant polydispersities are predicted, but the predicted profile lies significantly lower than the experimental data. The agreement is better for the MA case, although once again the sharp increase at the very beginning is observed, and the increase on DI at the end of the polymerization seems to be captured later than it occurs in the actual system.

Figures 10 and 11 show the effect of initiator concentration on conversion and weight average molecular weight, respectively, at 40 min of reaction time, at the conditions shown in the figure captions. As expected, it is observed that a higher monomer conversion and a lower weight average molecular weight are obtained, at a given time (in this case, at 40 min), when the concentration of initiator is increased. Model predictions are slightly
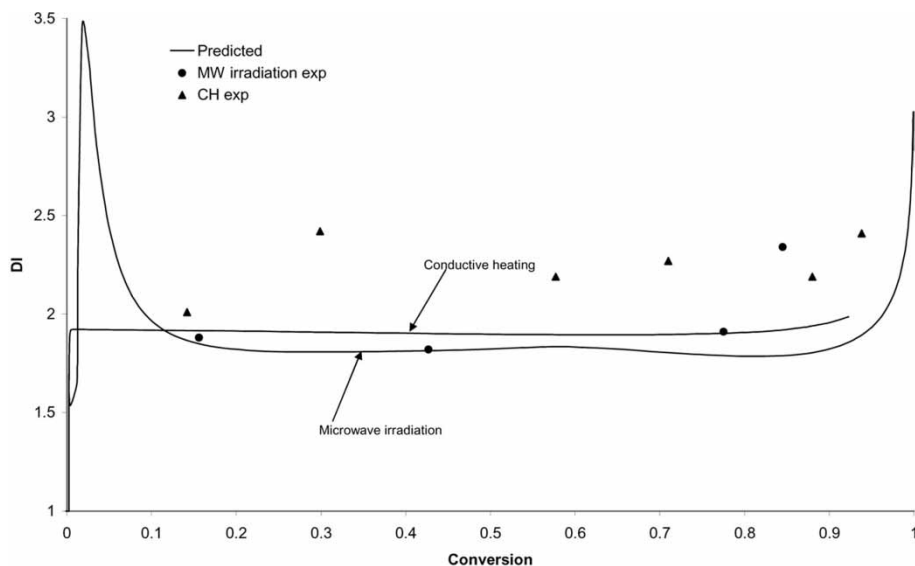
Figure 9. Comparison of predicted profiles of polydispersity index (DI) vs. conversion, against experimental data of Zhu et al. (5), in emulsion polymerization of styrene with conductive heating (CH) and microwave activation (MA or MW).

higher than the experimental data in both cases, but overall, the agreement between model predictions and the experimental data of Zhu et al. (5) is very good.

Figure 12 shows predicted profiles obtained with Predici$^{®}$ and experimental data of Correa et al. (4) for the microwave activated emulsion polymerization of styrene, at
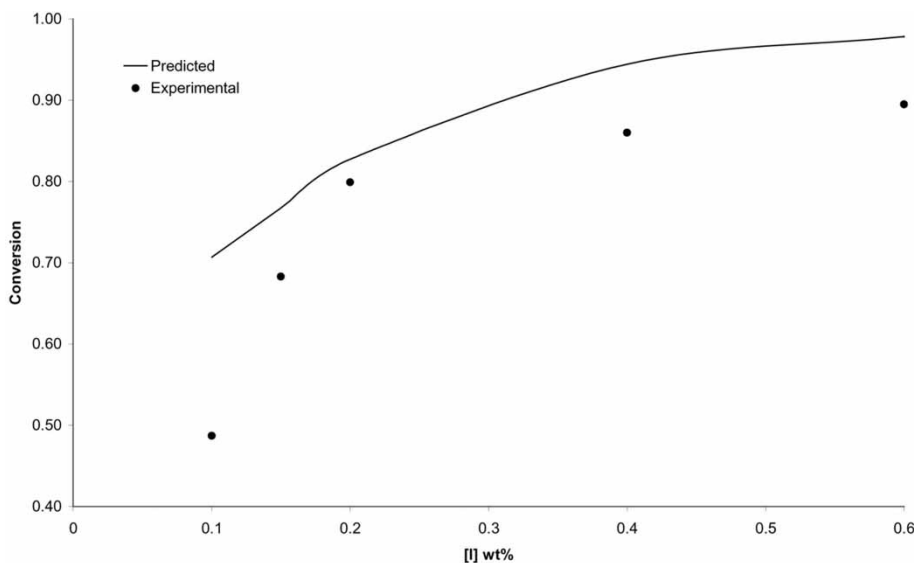

Figure 10. Effect of initiator concentration on monomer conversion at 40 min in microwave activated emulsion polymerization of styrene. P = 120 kW, reaction time: 40 min., and T = 70°C. Model predictions with Predici$^{®}$ (solid line) against experimental data (●) of Zhu et al. (5).
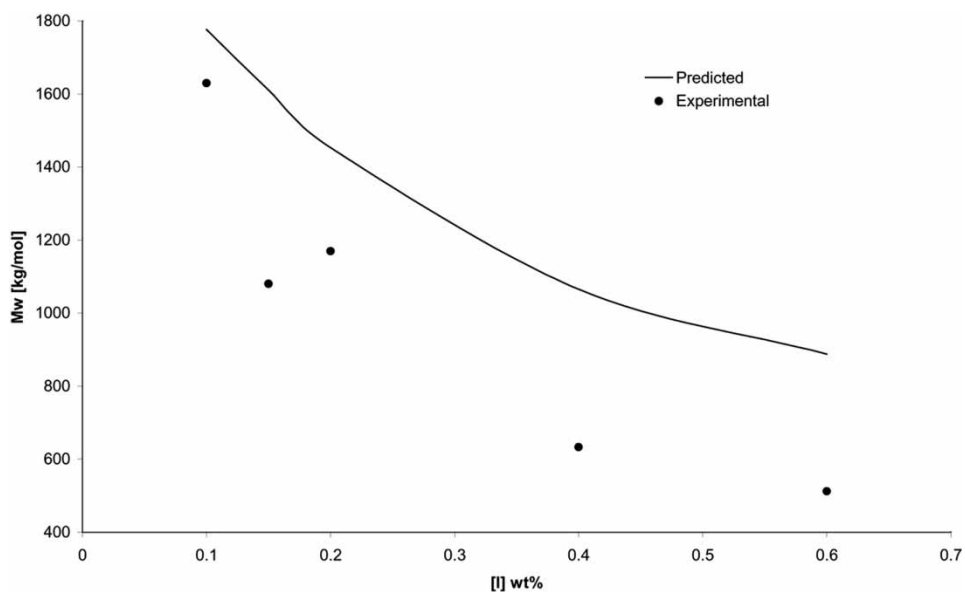
Figure 11. Effect of initiator concentration on weight average molecular weight at 40 min in microwave activated emulsion polymerization of styrene. P = 120 kW, reaction time: 40 min., and T = 70°C. Model predictions with Predici® (solid line) against experimental data (●) of Zhu et al. (5).
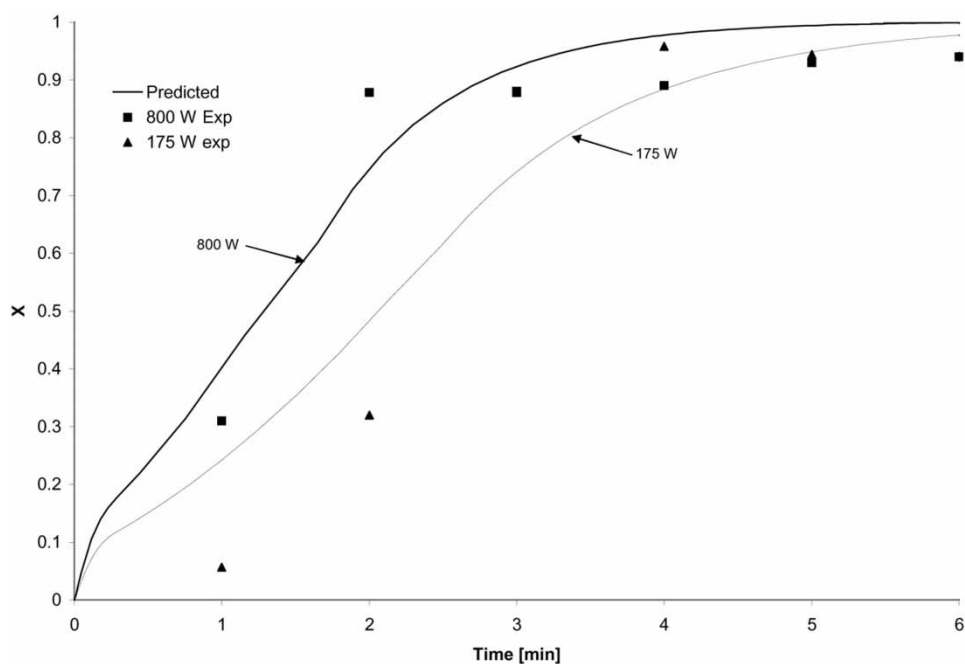

Figure 12. Effect of irradiation power (800 W and 175 W) on polymerization rate. Initiator: 0.16 wt%, monomer-to-water volume ratio: 1 : 3., T = 70°C. Experimental data from Correa et al. (4).

two values of the irradiation power (175 and 800 W). As expected, the polymerization proceeds faster when the irradiation power is increased. The predicted values of monomer conversion, in the low conversion region, are significantly higher than the experimental data, for the lower value of irradiation power, although the agreement is fairly good. In the case of the higher value of irradiation power, the agreement at low and intermediate conversions is very good, and a small discrepancy is observed at high conversions, the model predictions being higher than the experimental data. Finally, Figure 13 shows the case of MA emulsion polymerization of styrene at 800 W (the higher value of irradiation power analyzed in Figure 12), but at a lower initiator concentration. As expected, the polymerization proceeds slower when the initiator concentration is decreased. The agreement between the calculated profile with Predici® and the experimental data shown in Figure 13 is again very good.

Conclusions

The emulsion polymerization of styrene activated by simultaneous microwave irradiation and conductive heating was successfully modeled using Predici®, the simulation package of CiT. Although the approach of Predici® to address multiphase polymerization systems is kinetic in nature, it was possible to reproduce experimental data with information available in the literature.

Although the true nature of microwave irradiated activation in emulsion polymerization is not continuous, i.e., the microwave source turns on and off twice per minute (3), thus being an intermittent process, the overall performance of the process is well captured assuming that the microwave irradiated activation is equivalent to that of chemical initiator of very high decomposition rate, or equivalently, using a high
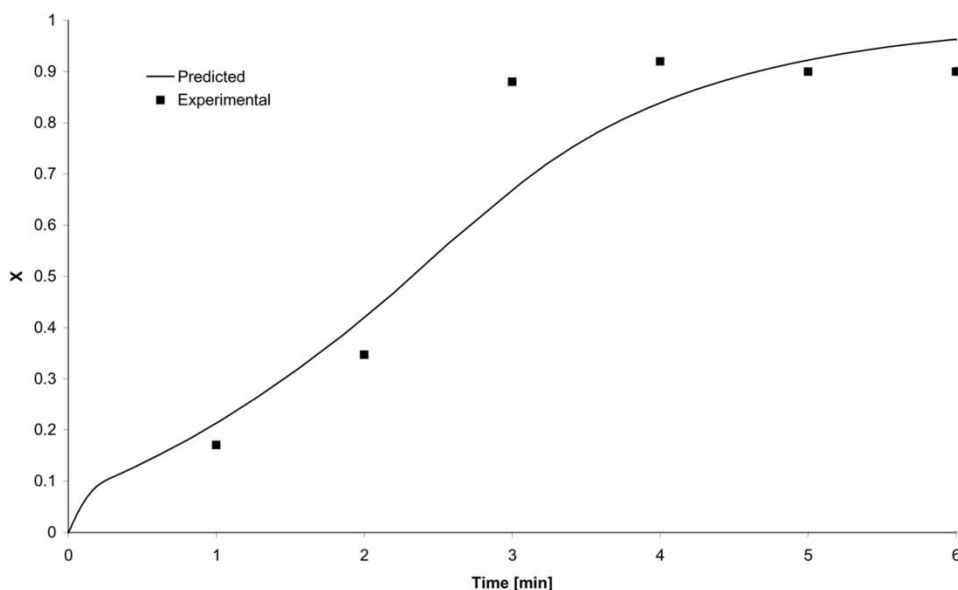

Figure 13. Conversion vs. time predicted profile against experimental data of Correa et al. (4) in MA emulsion polymerization of styrene. Power: 800 W, initiator: 0.04 wt%, monomer-to-water volume ratio: 1:3, T = 70°C.

concentration of it, so it is considered to be proportional to the intensity of microwave irradiation.

The agreement for polymerization rate and molecular weight development between model predictions and experimental data from different laboratories, covering a wide range of experimental conditions, was good. This is remarkable, considering that most kinetic rate constants were taken from the literature. Only the kinetic rate constant for "monomer precipitation" was needed to be fine-tuned, in order to reproduce the experimental data from the three different research groups, in the cases of microwave irradiation and conductive heating, with the same value of k_{pre} at a given temperature.

Nomenclature

$[I]$	Initiator concentration $(mol\,L^{-1})$
$[M]$	Monomer concentration $(mol\,L^{-1})$
C_p	Latex-phase solubility $(mol\,L^{-1})$
C_w	Aqueous-phase solubility $(mol\,L^{-1})$
E_{abs}	Absorbed energy $(J\,s^{-1})$
E_{sup}	Supplied energy $(J\,s^{-1})$
F	Initiator efficiency
f_r	Microwave irradiation efficiency
I	Initiator
$I^\bullet$	Primary radical from initiator
$I_p^\bullet$	Oligomeric radical from initiator, in latex phase
K_{eq}	Equilibrium constant for monomer partitioning ($=C_w/C_p$, Gao and Penlidis (2))
k_{coa}	Kinetic rate constant for coagulation of monomer droplets $(L\,mol^{-1}\,min^{-1})$
k_d	Kinetic rate constant for initiator decomposition (min^{-1})
k_{dp}	Kinetic rate constant for termination by disproportionation in polymer particle $(L\,mol^{-1}\,min^{-1})$
k_{fast}	Kinetic rate constant rate for the "fast" consumption of I_p^* $(L\,mol^{-1}\,min^{-1})$
k_{fm}	Kinetic rate constant for chain transfer to monomer $(L\,mol^{-1}\,min^{-1})$
k_{ir}	Kinetic rate constant for microwave activation $(L\,mol^{-1}\,min^{-1})$
k_p	Kinetic rate constant for propagation $(L\,mol^{-1}\,min^{-1})$ (i > 3)
k_{p1}, k_{p2}, k_{p3}	Kinetic rate constant for propagation in aqueous phase $(L\,mol^{-1}\,min^{-1})$, i-mer, i = 1, 2, 3
k_{pht}	Kinetic rate constant for oligomer transfer from aqueous to latex phases $(L\,mol^{-1}\,min^{-1})$
k_{pre}	Kinetic rate constant for monomer precipitation (min^{-1})
k_{tc}	Kinetic rate constant for termination by combination in polymer particles $(L\,mol^{-1}\,min^{-1})$
M_{aq}	Monomer in water phase
M_n	Number average molecular weight $(kg\,mol^{-1})$
M_p	Monomer in latex phase
M_{pre}	Monomer precipitated
M_w	Weight average molecular weight $(kg\,mol^{-1})$
P_r	Dead polymer of chain length r

R	Ideal gas constant
$R_1^\bullet$, $R_2^\bullet$, $R_3^\bullet$	Free radicals with 1, 2 and 3 monomer units, respectively
$r_{I,mv}$	Rate of initiation under microwave activation
r_{mv}	Rate of microwave absorbed radiation ($J\,kg^{-1}\,s^{-1}$)
$R_r^\bullet$	Live polymer of chain length r
T	Temperature (K)
x	Monomer conversion
z	Critical chain length which water phase radicals can be irreversibly absorbed

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