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### Effect of Microwave Activation on Polymerization Rate and Molecular Weight Development in Emulsion Polymerization of Methyl Methacrylate

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# Effect of Microwave Activation on Polymerization Rate and Molecular Weight Development in Emulsion Polymerization of Methyl Methacrylate

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*Polymerization rate and molecular weight development experimental results for the emulsion polymerization of methyl methacrylate (MMA), in the presence of potassium persulphate (PPS) as initiator, and activated with a 50 W microwave source, are reported. The polymerization kinetics of the microwave activation experiment (MA) was compared against a traditional conductive heating (CH) polymerization reaction. The number average molecular weights,  $M_n$ , of the polymer samples obtained with microwave activation were significantly higher than those obtained from conductive heating. These high values of  $M_n$  were obtained from the beginning of the polymerization reaction. Polydispersity index (PDI) values in the range of 1.18 to 1.83 were obtained in the microwave irradiated samples. These values are lower than those produced by conventional emulsion polymerization of styrene and other vinyl monomers, and resemble the PDI values obtained in controlled-radical polymerization processes. Polymer particles of submicron size (60 to 100 nm) were obtained.*

**Keywords** microwave irradiation, emulsion polymerization, poly(methyl methacrylate)

## Introduction

The use of dielectric heating as an alternative to conductive heating in high technology chemical processes and polymer synthesis has generated interest in the scientific community, due to the several recognized potential benefits of microwave irradiation. Some of the advantages are the following: drastic reduction of reaction times, higher yields, enhanced reaction selectivity, lower thermal decomposition of products, and

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more control over the safety operational conditions of the process. The use of microwaves in the chemical laboratory has proven to be a good power source to reduce the time and cost for the preparation of samples, needed in large numbers, for analytical tests.

The state of the art and future perspectives of microwave assisted polymer synthesis has been recently reviewed by Wiesbrock et al. (1) Although the number of publications on microwave-assisted polymerization has grown in an almost exponential manner since the 1960's (1), the field of microwave-assisted emulsion polymerization is still developing, with the main contributions coming from a few groups (2–11).

Important efforts have been oriented towards understanding and separating the thermal and “specific” interactions of the microwaves with the initiator and monomer molecules, since, for instance, at the same initiator concentration, the number average molecular weight,  $M_n$ , obtained under microwave activation (MA) is 1.1–2 times higher than under conductive heating (CH) (7). It is possible that, under high power irradiation, the molecules of initiator and monomer could rotate and oscillate at very high speed, then becoming polarized and deformed. This could enhance the monomer reactivity and facilitate the formation of polymer molecules. The result is a strong auto-acceleration effect (7). These and other issues require further research studies to be carried out.

In this contribution, the emulsion polymerization of methyl methacrylate (MMA), in the presence of potassium persulphate (PPS) as initiator, and using one power condition for microwave irradiation (50 W), is studied. The polymerization kinetics of the microwave experiment (MA) is compared against a traditional conductive heating (CH) polymerization reaction. Our attention is focused on elucidating the effect of the microwave-irradiation activation on the molecular weight, and the molecular weight distribution, in methyl methacrylate (MMA) emulsion polymerization, calculating the polymerization rate at 50°C, and analyzing the effect of the initiator initial concentration on the polymerization rate, and the molecular weight development.

## Experimental

### Materials

The MMA monomer was purified by vacuum distillation prior to the start of the polymerization experiments in order to eliminate inhibitor and impurities. Water was deionized by filtration through a Millipore cartridge. Oxygen was eliminated from water by gently heating below the boiling point of water for 10 min, just before the preparation of the monomer emulsion.

Anionic type sodium dodecyl sulphate (SDS) emulsifier and the initiator, potassium persulphate (PPS), were used directly as received from the producers. All the solvents used in the purification and characterization of our samples were of chromatographic grade, and did not require further purification.

### Emulsion Preparation

The monomer emulsion was prepared at room temperature. In a typical procedure, 1.668 g of sodium dodecyl sulfate (SDS) were dissolved in 400 mL of deionized water. Then, 39 mL of MMA monomer were slowly poured and stirred for 1 h in the aqueous surfactant solution in order to obtain a stable emulsion. A constant, soft nitrogen flow was maintained throughout the experiment in order to eliminate the presence of oxygen in the flask.

**Table 1**

Emulsion polymerization of MMA activated by microwaves with 50 W source power, at 50°C. Data for polymer yield 85% or higher, after 10 min of irradiation

Experiment	PPS conc (g L <sup>-1</sup> )	M <sub>w</sub> × 10 <sup>-3</sup> (Da)	M <sub>n</sub> × 10 <sup>-3</sup> (Da)	PDI	R <sub>p</sub> × 10 <sup>3</sup> (mol L <sup>-1</sup> s <sup>-1</sup> )
P1	0.28	456.7	346.5	1.31	0.31
P2	0.563	535.2	429.9	1.25	2.78
P3	0.844	503.7	302.6	1.66	8.59
P4	1.125	502.9	274.2	1.83	9.40
P5	1.406	503.7	301.6	1.67	10.23
P6 <sup>a</sup>	1.125	533.4	261.6	2.04	6.85 × 10 <sup>-5</sup>

<sup>a</sup>Conductive heating for 120 min.

The required amount of initiator (PPS) was supplied to each recipe according to the experimental plan, shown in Table 1.

### Polymerization

In a 1 L glass beaker, packed with vermiculite, ten test tubes filled with water were placed in a circular arrangement. A 20 mL tube with the previously prepared MMA emulsion was placed at the center. In order to monitor the reaction temperature, a thermocouple was inserted in the emulsion tube. Stainless steel bearing balls helped to maintain the emulsion stability by shaking the test tube. For the polymerization kinetics experiments, some of the water tubes were replaced by tubes filled with MMA emulsion. Wiesbrock et al. (1) have questioned the direct comparison between microwave and conventional heating in the experiments performed by Palacios and Valverde (2), arguing that temperature in the reaction mixtures might not be the same. The direct measurement of temperature in the reaction mixture, and the use of moderate polymerization temperatures (50°C), minimize those concerns.

In these experiments, a Portland DMR-41 microwave oven was used. The source had the following characteristics: wave length of 12.2 cm, 2450 MHz, and 50 W in the magnetron. The oven had a digital temperature-time control panel. The microwave oven was programmed to keep a constant temperature of 50°C. The temperature was measured in the polymerization sample, with a thermocouple, and controlled to  $\pm 2^\circ\text{C}$ . The reaction times were controlled to  $\pm 3$  s. The microwave source turned on and off twice per minute. This frequency maintained a constant temperature in the system.

The polymerization kinetics was followed by taking out emulsion samples from the oven at different reaction times. After the polymerization time was completed, each sample was quenched to 0°C in an ice-water bath. Then, two drops of a 0.5 w% aqueous solution of hydroquinone were added to fully stop the polymerization. The polymer emulsion samples were stabilized and homogenized in a sonicator, in order to eliminate the possibility of cluster formation. In a 10 mL glass vial, 2 mL of the reacted emulsion were separated and weighed. To precipitate the poly(methyl methacrylate) (PMMA), 5 mL of methanol were added. The polymeric material was separated by filtration, and the residual monomer contained in the liquid phase was analyzed by gas

chromatography, following the procedure described previously to calculate monomer conversion (2).

A second emulsion sample of 5 mL was poured into an aluminum dish, and dried for 36 h at 35°C in a vacuum oven. The PMMA solid samples were purified by solution-precipitation from THF/methanol. The residual solid polymer was weighed to calculate the polymer yield. The same procedure was repeated for the different reaction times.

### Polymer Characterization

The average molecular weights and the molecular weight distributions of the produced PMMA samples were obtained with a Waters HPLC apparatus. Tetrahydrofuran (THF) was used as the eluent, and a flow rate of 1.0 mL/min was used in the two Ultrastragel columns. Polystyrene standards were selected for calibration in our experiments at 30°C.

The glass transition temperature ( $T_g$ ) of the samples was determined by calorimetric analysis (CA), in a DuPont 990 differential scanning calorimeter (DSC). The sample tests were run under nitrogen, at 40 mL/min, and at a heating rate of 10.0°C/min.

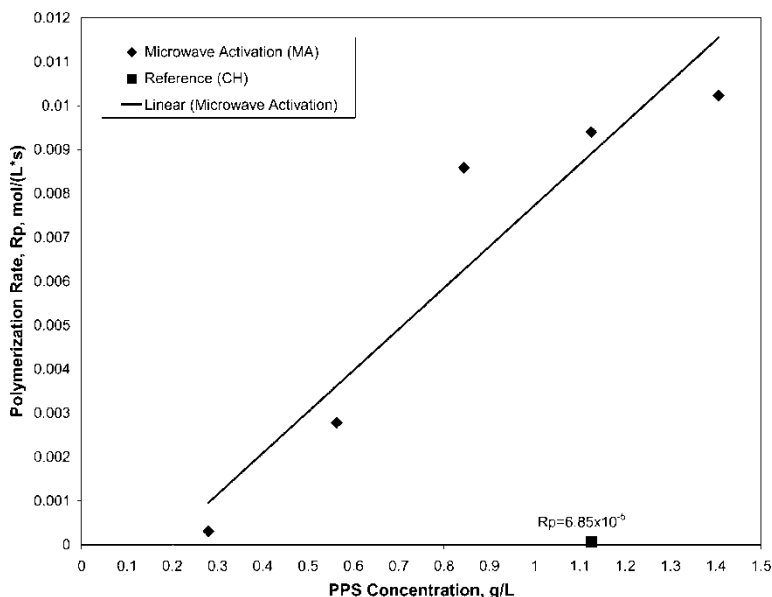
The polymer particle size was measured in a He/Ne, 4 mW Coulter Counter. Calibration was made with PS standards, 10 to 100 nm in diameter, in water as eluent.

### Results and Discussion

Table 1 summarizes the results on number and weight average molecular weight, and polymerization rate for the polymerization of MMA activated by a 50 W microwave source power, at 50°C, after 10 min of irradiation, and at polymer yields of 85%, or higher. The effect of PPS initiator concentration is analyzed. Figures 1 to 3 show the same information in graphical form.

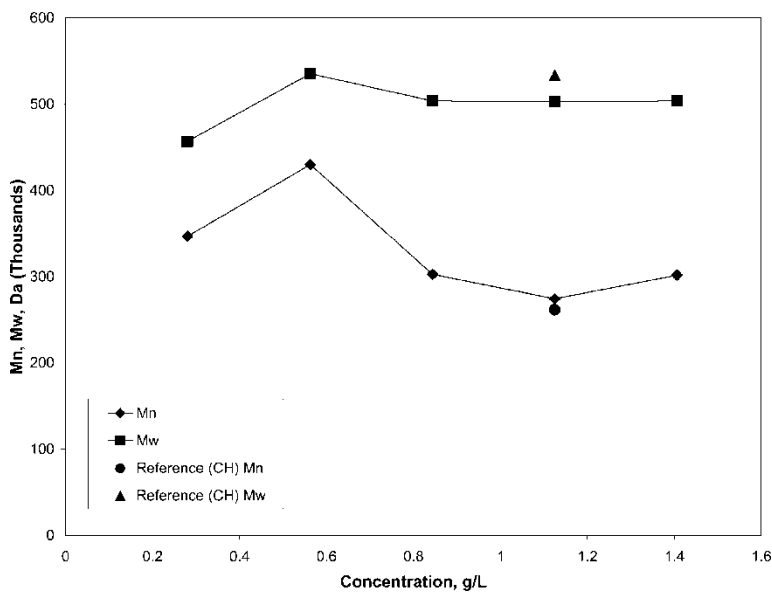
In Figure 1, it is observed that the polymerization rate increases linearly with respect to the concentration of PPS. The polymerization proceeds more than two orders of magnitude faster in the microwave activated experiments, as compared to the conductive heating reference experiment (see experiments P4 and P6, which are fully comparable, since they proceed at the same PPS concentration). Calculation of the polymerization rate,  $R_p$ , was carried out following the procedure described in Palacios and Valverde (2). A value of 3 for the initial slope of a plot of  $\ln(R_p)$  vs.  $\ln([I])$  was obtained, which is high, compared to the value of 1.5, reported for MA emulsion polymerization of styrene (2). This result indicates that the MA emulsion polymerization of MMA is faster than the corresponding rate for styrene. A comparison of the ratio of  $R_{pMA}/R_{pCH}$  for styrene and MMA, which are of 26.33 and 137.23 (calculated for MMA using experiments P4 and P6, from Table 1), respectively, shows that the activation obtained by microwave irradiation is much higher for the emulsion polymerization of MMA than it is for the emulsion polymerization of styrene.

Figure 2 shows that the number average molecular weight,  $M_n$  slowly decreases as the concentration of PPS is increased. The value at 0.563 g L<sup>-1</sup> of PPS concentration (experiment P2) shows the highest value of  $M_n$  from all the samples. This would suggest that there is an optimal value of concentration of PPS, which produces the highest molecular weight, and the lowest PDI (see the value of PDI for experiment P2, in Table 1). However, there is also the possibility of that data point being an outlier, a (point not being part of the population). If that was the case, the trend observed in Figure 2 would suggest that  $M_w$  remains almost constant, and  $M_n$  decreases linearly,

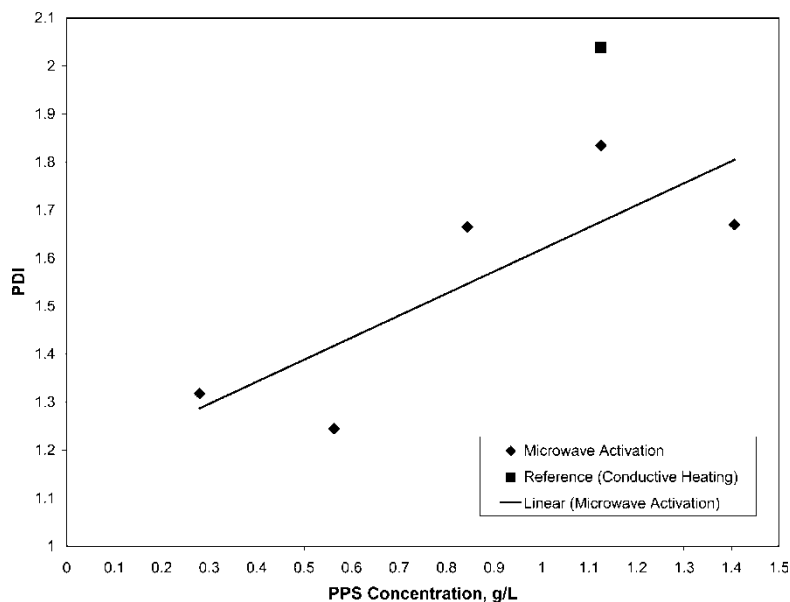


**Figure 1.** Effect of the initiator concentration on the polymerization rate of MMA emulsion polymerization activated with a 50 W microwave source, at 50°C and 20 min of exposition time.

with PDI showing living-like behavior at low concentrations of PPS. When PDI is plotted against a PPS concentration, as in Figure 3, the behavior seems to be clearer. There seems to be a linear trend, with the lowest final PDI value obtained at the lowest PPS concentration. Even though PDI increases with PPS concentration for the microwave activated



**Figure 2.** Microwave activated emulsion polymerization of MMA. Effect of initiator concentration on the number and weight average molecular weights,  $M_n$  and  $M_w$ .



**Figure 3.** Effect of initiator concentration on the polydispersity index, PDI, of MMA emulsion polymerization with microwave activation (MA).

experiments, all the cases are much faster than the CH reference case, and the highest observed PDI and the lowest  $M_n$  values for the MA experiments are lower and higher, respectively, than the corresponding values for the CH reference case.

As mentioned above, the runs with low initiator content show particularly low PDIs at high conversions, almost as low as the ones obtained in controlled/“living” radical polymerization (CRP) processes (12), and certainly lower than the lower theoretical limit for conventional bulk and emulsion free-radical polymerization processes. These low values of polydispersity are characteristic of “living” systems, and might be explained by the fast initiation rate, promoted by the high energy associated to the microwave irradiation. It may also be possible that the propagation rate is favored over the bimolecular termination rate, thus making the system more “living”-like.

It is uncertain if the microwave irradiation could promote some sort of reversible activation/deactivation process, similar to the ones known in CRP processes (12). Although Zhu et al. (7) and Hu et al. (9) studied the emulsion polymerization of MMA with microwave activation, they did not report measurements of weight average molecular weight. Therefore, it seems that this “living”-like behavior had not been observed before in MA emulsion polymerization.

In order to compare the evolution of the polymerization rate between MA and CH emulsion polymerizations as time proceeds, several measurements of monomer conversion vs. time, and their corresponding  $M_n$  and  $M_w$  values, at the conditions of experiments P4 and P6, were obtained. Table 2 shows the results in tabular form, whereas Figures 4 to 7 show the results in graphical form.

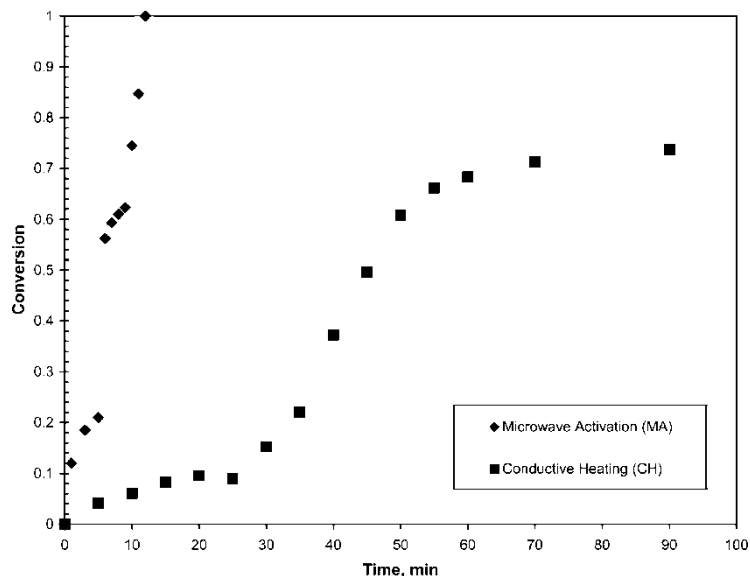
As observed in Figure 4, the polymerization rate is much faster in the MA case. Total monomer conversion in the MA case is achieved in 12 min, whereas in the CH case, a limiting conversion lower than 80% is reached from about 50 min of reaction time. It is well known that microwave energy is absorbed by molecules in a magnitude proportional

**Table 2**

Kinetic data for experiments P4 and P6, microwave activation and conductive heating. Initiator concentration of 1.125 g/L, at 50°C

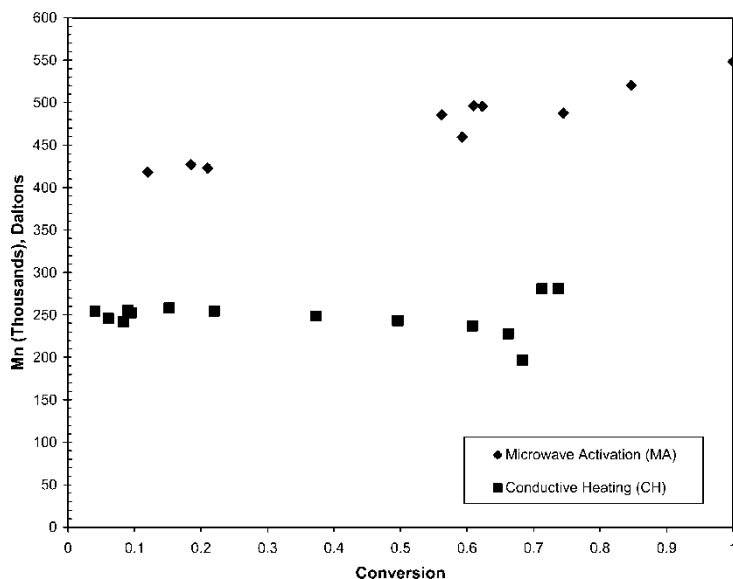
P4 microwave activation					P6 conductive heating				
T (min)	% Conv	$M_w \times 10^{-3}$ (Da)	PDI	$D_{\text{part}}$ (nm)	T (min)	% Conv	$M_w \times 10^{-3}$ (Da)	PDI	$D_{\text{part}}$ (nm)
1	12.0	485	1.16	63.0	5	4.1	321	1.26	48
3	18.5	504	1.18	65.0	10	6.1	317	1.29	49
5	21.0	520	1.23	65.5	15	8.3	315	1.30	51
6	56.2	607	1.25	67.0	20	9.5	316	1.25	50
7	59.3	625	1.36	67.8	25	9.0	322	1.26	51
8	61.0	680	1.37	69.1	30	15.2	320	1.24	52
9	62.3	699	1.41	71.0	35	22.0	321	1.26	52
10	74.5	780	1.60	76.0	40	37.3	321	1.29	54
11	84.7	890	1.71	80.0	45	49.6	319	1.31	56
12	100.0	987	1.80	97.0	50	60.8	325	1.37	57
					55	66.2	335	1.47	58
					60	68.3	338	1.72	60
					70	71.3	551	1.96	61
					90	73.7	588	2.09	63



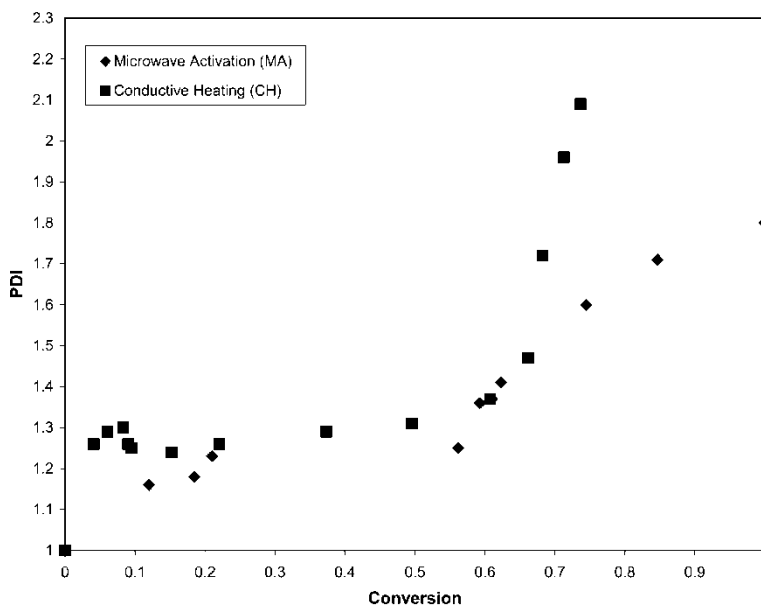


**Figure 4.** Comparison of monomer conversion between microwave activation and conductive heating, for the emulsion polymerization of MMA, at 1.125 g/L of PPS and 50°C.

to their dielectric constant,  $E$ . In a microwave initiated emulsion polymerization, the energy goes preferentially to water and monomer molecules, in that order. Since water contributes to the system with the largest amount of mass, the microwave energy will produce a local sensible increment in temperature and thus, a reduction of the local

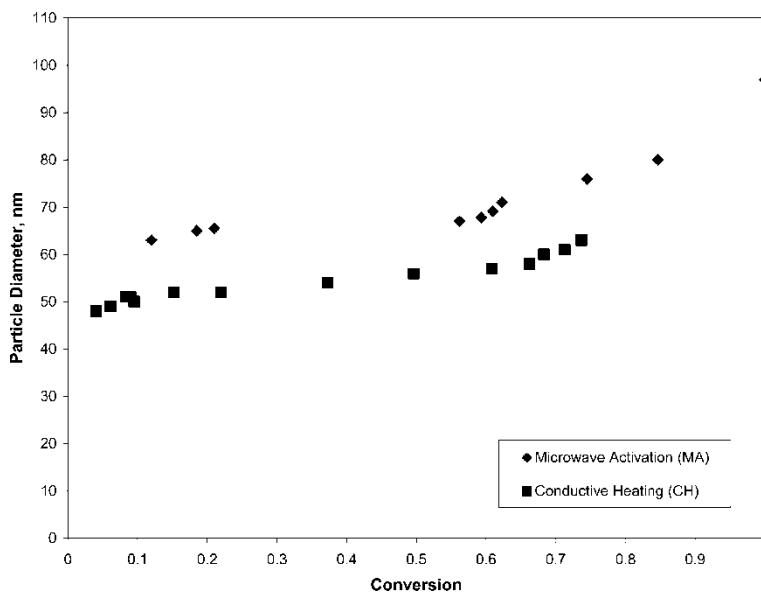


**Figure 5.** Comparison between number average molecular weight,  $M_n$ , for the microwave activation (MA) and conductive heating (CH) processes, of MMA emulsion polymerization, at 1.125 g/L of PPS and 50°C.



**Figure 6.** Evolution of the polydispersity index, PDI, for MA and CH emulsion polymerization of MMA, at 1.125 g/L of PPS and 50°C.

viscosity of the aqueous continuous media. Under these conditions, primary radicals generated from the initiator and MMA monomer molecules will diffuse rapidly to the micelles, the reaction site. Once inside a micelle, the consumption of the primary radicals, through monomer propagation, will occur in an extremely short time, in a



**Figure 7.** Evolution of polymer particle size, for MA and CH emulsion polymerization of MMA, at 1.125 g/L of PPS and 50°C.

large number of sites at the same time. Then, a very fast nucleation, both homogeneous and micellar, will occur and lead to the appearance of a large number of oligo-radical particles, with a constant and fast supply of more MMA monomer.

Figure 5 shows a comparison of the number average molecular weight,  $M_n$ , versus conversion, for MA and CH emulsion polymerizations of MMA. The corresponding profiles of PDI vs. conversion are shown in Figure 6. It is observed in Figure 5 that  $M_n$  is fairly constant during all the polymerization process in the CH case, whereas it increases linearly with a small slope in the MA case. Although the line representing  $M_n$  vs. conversion for the MA case does not start from the origin, the fact that a linear relationship is observed and that PDI values between 1.15 and 1.3 were obtained in the low and intermediate conversion ranges (up to a conversion of about 0.55, where PDI starts increasing steadily up to a value of 1.8, at 100 percent monomer conversion), suggests that some sort of pseudo-living behavior is present in the MA case.

In Figure 6, it is clearly observed that low polydispersities are obtained in the MA case, from the beginning of the polymerization up to about 55% monomer conversion. After that, the PDI increases with a positive and then negative slope, up to a value of 1.8, at 100% of monomer conversion. It was rationalized before that in the case of MA, the primary radicals and the monomer molecules would migrate very rapidly to the polymer particles, or nucleate new particles, so that propagation would proceed fast, and termination would not be affected much by diffusion-controlled barriers, at least at low and intermediate conversions. As explained before, the fact that MA provides fast initiation rates, combined with fast propagation rates, and moderate bimolecular termination rates, would promote the creation and growing of macromolecules similar in size, similar to the conditions found in typical living polymerizations, with PDI values lower than 2 (usual limit in emulsion polymerization), and even lower than 1.5 (theoretical limit if all termination proceeded by recombination).

However, Figure 6 also shows the profile of PDI vs. conversion for the CH case, where no irradiation is used, and some unusual behavior was obtained. It is observed that PDI increases dramatically at about the same conversion as in the MA case (around 55% monomer conversion), but what is strange is that the PDI values at low and intermediate conversions, although higher than the ones obtained in the MA case, are also lower than 1.5 (around 1.3); namely, that a "living-like" behavior is also observed in the CH case. It is well known from the literature in emulsion polymerization, that the PDI values obtained on free-radical emulsion homopolymerizations are usually higher than the corresponding mass and solution situations, with PDI values closer to 2, or higher, being common (13). However, it is also known that if interval II of emulsion polymerization (when the radical arrival rate should be fairly constant, and the drift in dispersion of the molecular weight distribution, MWD, is eliminated) covers a sufficient amount of the conversion, then emulsion polymerization can result in a more narrowly distributed polymer than a corresponding bulk or suspension polymerization (14). Therefore, the PDI values around 1.3 in the CH experiments at low and intermediate conversions would suggest that interval II of emulsion polymerization lasts up to about 55% of monomer conversion, and that termination by combination might dominate over termination by disproportionation, at the polymerization conditions used in this study (both CH and MV).

Particle size,  $D_p$ , vs. conversion profiles for the MA and CH experiments chosen for our kinetic study (P4 and P6, respectively), are shown in Figure 7. It is observed that the particle diameters obtained with MA are 10 to 15 nm larger than the particles obtained with CH. Particle size remains fairly constant for both cases (MA and CH), at values of

around 50 and 65 nm, respectively, up to about 60% of monomer conversion. After that, particle size increases in a near-linear fashion, for the MA case, up to a final size (at 100% monomer conversion) of around 100 nm. The fact that the particle size remains almost constant up to a conversion of 0.55–0.6, supports our previous explanation about the low PDIs, attributed to the time duration of stage II of emulsion polymerization (13). It is also interesting to note that the particle sizes obtained in our experiments are smaller than the MMA particles synthesized by Hu et al. (9), and a bit bigger than the smallest particles reported by Bao and Zhang (11), which shows the potential of microwave emulsion polymerization to easily synthesize materials useful for nanotechnology applications.

Our experiments were carried out with a SDS concentration of  $4.17 \text{ g L}^{-1}$ . This concentration is well above the critical micellar concentration (CMC) of SDS, which is of  $2 \text{ g L}^{-1}$ . Therefore, the dominant nucleation mechanism under the conditions of our experiments might have been micellar nucleation. Under this condition, the calculated surface area is larger than that of the average surface of the final latex particles. Calculation of the potential surface coverage by SDS in our system, for experiments P4 and P6, allowed us to estimate the number of particles,  $N_p$ , and the average particle surface area,  $S_A$  ( $\text{cm}^2$ ), which are ( $0.69 \times 10^{17}$  particles,  $2 \times 10^7 \text{ cm}^2$ ) and ( $1.9 \times 10^{17}$  particles,  $2.4 \times 10^7 \text{ cm}^2$ ), respectively.

The glass transition temperatures of our samples, obtained by microwave activation (MA) and conductive heating activation (CH) emulsion polymerization, were of  $100^\circ\text{C}$  in both cases, which indicates that the microwave activation (MA) has little effect on the calorimetric properties of PMMA.

## Conclusions

Microwave activation in emulsion polymerization of MMA produces a polymer of similar and even better properties, as conventional conductive heating emulsion polymerization, with much faster (more than two orders of magnitude) polymerization rates.

A polymer of higher number average molecular weight,  $M_n$ , and lower polydispersity, PDI, can be obtained with microwave activated (MA) emulsion polymerization, as compared to conductive heating (CH) emulsion polymerization. The values of PDI reached at low and intermediate monomer conversions can be as low as those obtained in controlled radical polymerization (CRP), which makes MA emulsion polymerization an interesting technique to produce a polymer of controlled microstructure. If MA is used in emulsion or miniemulsion CRP processes, the possibilities of producing materials of controlled microstructures in reasonable or even short times are interesting and promising.

The particle sizes obtained in MA emulsion polymerization of MMA are slightly larger than the ones obtained using CH activation. However, it is possible to produce submicron size particles (60 to 100 nm) fairly easily. A compromise between polymerization rate and particle size could be established, in order to optimize process conditions.

The area of microwave-assisted chemical synthesis, and in particular polymer synthesis, is attracting the interest of the scientific community, because of the many advantages and potential uses of this technique. Further research studies are needed in order to better understand the activation process, and to develop and propose commercial processes.

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