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Emulsion polymerization in a microwave reactor

R. Correa[a],*, G. Gonzalez[a] and V. Dougar[b]
[a]*Department of Chemical Engineering, Universidad Industrial de Santander, A.A. 678 Bucaramanga, Colombia*
[b]*Department of Physics, Universidad Industrial de Santander, A.A. 678 Bucaramanga, Colombia; revised 5 May 1997)*

Interest continues to grow concerning the application of microwave heating in chemical processes. This study shows that polymerization reactions such as emulsion polymerization in a polar solvent can be carried out rapidly and conveniently using microwave heating in glass reactors. It was found that a significant saving of energy and time was possible in the preparation of polystyrene. The heating rate was found to be influenced by the monomer-to-water ratio, magnetron power, the volume of the reaction mixture and the geometry of the container. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Microwave radiation is different because heat is generated in the material itself instead of externally. The dielectric properties which govern the rate of internal heating may vary widely in magnitude among the various constituents in a product, and are also a function of temperature. The temperature profile at a given time in a microwave-heated material will depend on the dielectric properties, specific heats and thermal conductivities of the material constituents[1].

The use of microwave radiation for the preparation and processing of polymers has received increasing interest due to significant advantages over the conventional thermal method in convection ovens. The use of microwave energy for the rapid synthesis of organic compounds was first reported in 1986. It was observed that organic reactions were dramatically accelerated by irradiating the reaction mixture with microwaves.

Literature reports that reactions of organic and organometallic compounds can be carried out with reaction rate enhancements of up to 1300 times. The acceleration in the reaction vessels, compared to normal reflux conditions, occurs because the increasing pressure developed in the reaction vessels causes superheating of the solvent.

Microwave heating results in considerable energy savings compared with conventional heating methods. Whittaker and Mingos[2] recently prepared a review of the application of microwave heating to chemical synthesis. This review summarizes the research work involving the direct application of microwave heating effects in chemical reactions. However, to our knowledge, there is no previous report about emulsion polymerization reactions carried out under microwave irradiation.

Microwave heating has not been found to alter appreciably the composition of products of a chemical reaction. While small differences in product ratios are reported in chemical reactions carried out under microwave irradiation and conventional heating, these have been explained as due to a thermal effect and can be attributed to the higher temperatures achieved in microwave reactions.

Akyel and Bilgen[3] have reported data on the microwave and radio-frequency curing of polymers. As they stated, there is not enough theoretical background to describe the thermodynamic behaviour of microwave-irradiated systems. They determined that the energy requirements for microwave curing are between 0.3 and 0.5 MJ kg^{-1} product. These values are about 10–20 times smaller than the respective values for conventional curing. They also estimated that the curing costs can be reduced by 55–72%.

Specific properties of the evaporation process in a cell located in a waveguide under microwave power were studied by Gillon *et al.*[4] It was found that the presence of the microwave field, apart from the direct warming of the irradiated volume, favours unsteady motion in the polar liquid. This phenomenon was attributed to auto-amplification of the thermal heterogeneity in liquids where the dielectric losses grow with temperature.

In this paper we present the results of using a bench-scale microwave polymerization reactor for the styrene (S) emulsion polymerization reaction. Under both microwave radiation and a conventional heating method, polystyrene (PS) was prepared by emulsion polymerization. The energy efficiency was increased by programming the power levels of the magnetron.

RESULTS AND CONCLUSIONS

Figure 1 shows the reactor system. The design considerations as well as the emulsion polymerization microwave reactor are described elsewhere[5]. The emulsion is prepared and added to the reservoir as shown in *Figure 1*. Once the pump is started, the emulsion flows through the reactor in a closed loop and simultaneously the magnetron is turned on. The conversion is followed by taking out samples of about 3–5 ml each time. To be aware of any pressure increases, a

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* To whom correspondence should be addressed

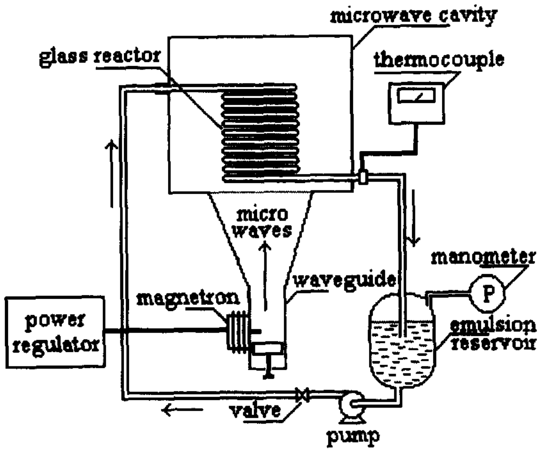

Figure 1 Experimental set-up for discontinuous operation of the reactor system

manometer was installed in the reservoir. This reactor can be used as a batch, semi-continuous or continuous reactor.

Microwave heating cycle

In order to examine the behaviour of the emulsion, several experiments using conventional microwave ovens were carried out. After several explosions of the containers we concluded that it is impossible, for the power levels tested, to heat the samples continuously. The principal reason for the explosions, we think, is the superheating of the system in a very short period of time (order of seconds). The water is superheated by the energy transported by the microwaves and this vapour vaporizes the monomer, leading to a considerable pressure increase. The higher the power used, the shorter the radiation time.

After all these experiments we decided to apply the microwave power but in a cyclic way; that is, as a rectangular pulse function. The sample is heated for 20 s (the effective time); after that, the microwave is turned off, leaving the sample for 600 s. The cycle is repeated several times until the desired final conversion is reached. Although several experiments varying those times were conducted, this paper reports data for only three effective times: 20, 30 and 60 s for two power levels, 175 W and 800 W.

Materials. Styrene monomer was washed with 10% aqueous sodium hydroxide solution, followed by water, dried overnight at 5°C with anhydrous sulfate ($100\,g\,l^{-1}$), and passed through an activated aluminium oxide column to remove the initiator. All other materials were used as received, including potassium persulfate initiator ($K_2S_2O_8$) and sodium lauryl sulfate as emulsifier. Double-distilled deionized water was used in the preparation of aqueous solutions.

Results. A latex was prepared using the recipe given in *Table 1*. For all the experiments the concentration range of materials was as follows: initiator 0.04–0.16 wt%, emulsifier 1.24%, monomer-to-water ratio 1:3, 1:16 and 2:3. The microwave power for the first set of experiments was 800 W, as shown in *Table 1*. The monomer-to-water ratio and the microwave power were changed for the second and third sets of experiments. PS was prepared by both methods, the conventional heating method and the microwave radiation method. The reaction temperature for both methods was 70 ± 4°C.

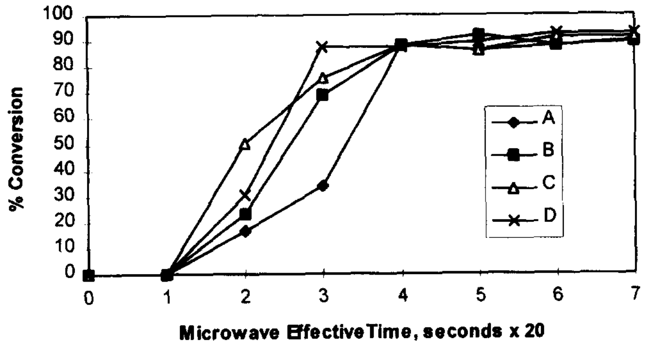

Figure 2 PS preparation by emulsion polymerization method under microwave irradiation

Microwave irradiation allows one to prepare PS by the emulsion polymerization technique in a very short period of time, about 140 s, as can be observed from *Figure 2*. In this figure, which includes the average of several experimental results, the x-axis represents the effective time in the vessel under microwave irradiation for four different initiator concentrations, while the y-axis represents the conversion. The reaction system was irradiated for 20 s, after which the power was shut off for 10 min. This cycle was repeated several times until conversion was about 90%.

The mechanism of energy transfer in microwave heating occurs by electric dipolar coupling of the radiation to permanent or induced dipole moments in the polymer, rather than by thermal conductivity as in the convection method. In this case, there are no dipoles in the polymer or monomer molecules, so water is the only substance in the reaction system that interacts strongly with the microwaves.

Table 2 includes the experimental results for the samples with higher initiator concentration. The magnetron power was only 175 W but the time of the system under radiation was increased to 60 s. The corresponding results of conversion as a function of the effective exposure time are shown in *Figure 3*. As expected, for higher power (800 W)

Table 1 Experimental conditions for samples A, B, C and D

	A	B	C	D
Initiator (%)	0.04	0.08	0.12	0.16
Emulsifier (%)	1.24	1.24	1.24	1.24
Monomer:water[a]	1:3	1:3	1:3	1:3
Power	800 W	800 W	800 W	800 W
Power on (s)	20 s	20 s	20 s	20 s
Power off (s)	600 s	600 s	600 s	600 s
Total time[b]	620 s	620 s	620 s	620 s

[a] Volume ratio.
[b] Time for each cycle.

Table 2 Experimental conditions for the second set of experiments using samples C and D

	C	D
Initiator (%)	0.12	0.16
Emulsifier (%)	1.24	1.24
Monomer:water[a]	1:3	1:3
Power	175 W	175 W
Power on	60 s	60 s
Power off	300 s	300 s
Total time[b]	360 s	360 s

[a] Volume ratio.
[b] Time for each cycle.

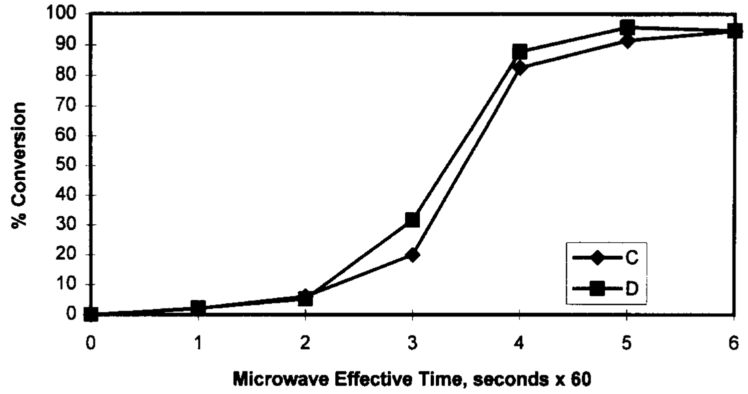

Figure 3 Ps preparation by emulsion polymerization method under microwave irradiation. Samples C and D as shown in *Table 2*

the monomer-to-polymer conversion is also higher, for the same period of time.

When the monomer-to-water ratio is changed, the conversion time is also changed. As shown in *Table 3*, the water content of the emulsion was increased for a power level of 800 W. A conversion of 100% was reached at 120 s using the power cycle included in *Table 3*, as can be seen from *Figure 4*. The effect of the presence of a polar material in higher quantity is evident.

When the monomer concentration is increased it is possible to observe a small effect on the curve of conversion *versus* microwave effective time, *Figure 5*. The power was 800 W, but the exposure time was decreased in order to avoid monomer evaporation. The operating conditions are included in *Table 4*.

TiO_2 effect

The reaction time was further decreased by the addition of titanium dioxide, as shown in *Figure 6*. There seems to be a particular time above which the conversion is independent of initiator concentration but dependent on the presence of titanium dioxide. This time is about 80 s, as shown in *Figure 2*, and about 60 s, as can be seen in *Figure 6*. We believe that such an effect is due to the high value of the dielectric constant of titanium dioxide. Besides, this material can be made to stay very close to the polymer particle, which means a better temperature distribution.

Conventional versus microwave

For comparison, we prepared PS by emulsion polymerization but using a conventional heating method, as mentioned before. As can be seen from *Figures 2, and 7*, the reaction time for the conventional heating method is about 70 times longer than that for the microwave irradiation method. It was also observed that the molecular weight of the polystyrene prepared by microwave radiation (M_w = 350 000) was 1.2 times higher than that of polystyrene prepared by the conventional heating method.

This study showed that chemical reactions such as emulsion polymerization in polar solvents can be carried out rapidly and conveniently using microwave heating. The period of time under microwave radiation for the sample was longer for lower power levels. The risk of explosion is high if over-long periods of time are used. It seems that the

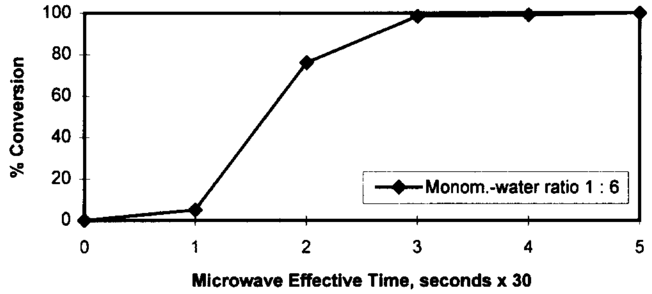

Figure 4 PS preparation by the emulsion polymerization method under microwave irradiation. The operational conditons are as shown in *Table 3*

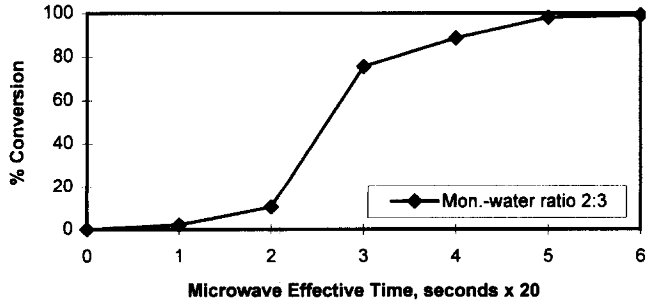

Figure 5 PS preparation by the emulsion polymerization method under microwave irradiation. The operational conditions are as shown in *Table 4*

Table 3 Experimental conditions for the second set of experiments using sample E

	E
Initiator (%)	0.12
Emulsifier (%)	1.24
Monomer:water[a]	1:6
Power	800 W
Power on	30 s
Power off	600 s
Total time[b]	630 s

[a] Volume ratio.

[b] Time for each cycle.

Table 4 Experimental conditions for the third set of experiments using sample F

	F
Initiator (%)	0.12
Emulsifier (%)	1.25
Monomer:water[a]	2:3
Power	800 W
Power on	20 s
Power off	600 s
Total time[b]	620 s

[a] Volume ratio.

[b] Time for each cycle.

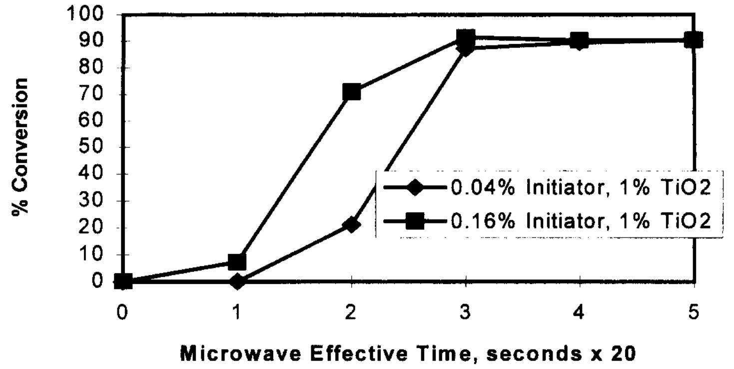

Figure 6 PS preparation under microwave irradiation but with 1% of TiO_2 added

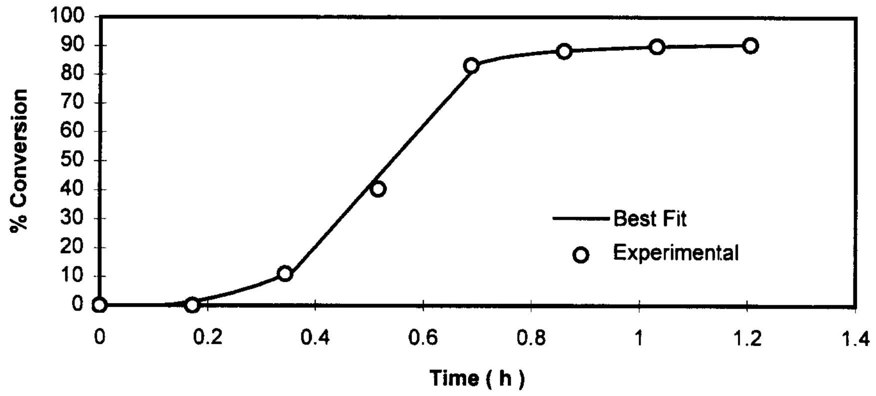

Figure 7 PS preparation by emulsion polymerization using conventional heating. The temperature was 70°C

dominant effect of the microwave on the emulsion polymerization of the styrene monomer is the thermal effect. This could be because more than 75% of the total volume is occupied by water, a molecule that interacts strongly with microwaves.

The heating rate was found to be influenced by the presence of ions in solution, the polarity, the volume of the reaction mixture and the geometry of the container. Further work is needed to expand comparisons such as this, and to understand the fundamental effects of microwaves on polymerizations. From the fundamental scientific point of view, an essential question regarding the application of microwaves in lieu of thermal energy is whether the microwave energy can alter the mechanism and kinetics of polymerization reactions. Such capability would undoubtedly have important implications in polymer manufacture.

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