Rapid Decomposition of a Cationic Azo-Initiator Under Microwave Irradiation

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ABSTRACT: Microwave-assisted decomposition of 2,2′-azobis(2-methylpropionamidine) dihydrochloride (or V50), a cationic azo-initiator, and emulsion polymerizations were performed and compared to reactions with conventional heating. Higher decomposition rate constants were found in microwave reactions. This was ascribed to the development of hot spots inside the reaction mixture, promoted by microwave irradiation. In polymerization reactions, microwave-promoted acceleration of the reactions. The effect of high power irradiation was also studied, using a pulsed method in which samples were repeatedly heated at constant power (500 or 1400 W), and cooled down by immersing in an ice bath. Rapid reactions were obtained, because a great amount of energy could be applied within short time intervals. The power level had no effect on the decomposed percentages and on the monomer conversion, and only affected the irradiation time. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1421–1429, 2010

Key words: microwave irradiation; initiator decomposition; emulsion polymerization; kinetics; V50

INTRODUCTION

Microwave irradiation is a heating method widely used in organic reactions. The microwave heating mechanism lies on the ability of the electric field to induce polarization of charges within the heated product. This polarization cannot follow the extremely rapid reversals of the electric field and induces heating of the irradiated media.[1–5] Moreover, this radiation also induces migration of the ions, and provides heating through ionic conduction mechanism.[1–3]

Although studies have listed several advantages of using microwave heating in organic chemistry, such as reduction in cycloaddition reaction times, modified selectivities in alkylation process, increased yields in cyclocondensation reactions[6] and acceleration of free-radical polymerization reaction rates,[7] some microwave effects have not been completely elucidated. In this sense, some authors defend that microwave irradiation can provide specific effects (either thermal or not purely thermal effects) generally connected to the selective absorption of microwave energy by polar molecules.[8–10]

Development of hot spots has been also pointed out as the origin of microwave effects. These localized microscopic high temperatures can be originated from differences in dielectric properties of materials or inhomogeneity of the applied electromagnetic field.[6,11,12] On a molecular scale, individual species or complexes are differently heated by microwave irradiation. So, the localized energy of the dipole or charged groups can be higher compared to the other species within these systems.[13] The contribution of hot spots to reaction rate enhancements in microwave driven chemical reactions has been reported in literature.[14–16] A study published about the effects of hot spots on reaction rate showed that a very small density of superheating areas is sufficient to induce a consequent rate enhancement, even if their effects are not detectable on average temperature.[17]

Concerning emulsion polymerization reactions, microwave heating has been extensively used to improve reaction rates.[7,18–23] Many published studies[18–20,24–27] support the idea that microwave effects on polymerization rates are ascribed to increase of initiator decomposition rates of microwave-promoted reactions. Investigations on the microwave-assisted initiator decompositions have already been

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carried out.[18–20,26–29] We have also studied the decomposition of an anionic initiator (potassium persulfate) with microwave heating.[29] However, to our knowledge, there are no published studies evaluating the decomposition of water-soluble azo-initiators and nonionic initiator (hydrogen peroxide) under microwave irradiation.

2,2′-Azobis(2-methylpropionamidine) dihydrochloride (V50) is a water-soluble azo-initiator that is particularly useful for the polymerization of water-soluble vinyl monomers to produce cationically-charged latexes. In this work, we evaluated the decomposition of V50 initiator under microwave and conventional heating conditions. The decomposition rate constants were determined for these reactions, to evaluate eventual microwave effects, such as improving yields or reducing reaction times. In addition, emulsion polymerization reactions of methyl methacrylate were performed under both heating methods, using V50 as initiator, to study the microwave effects on polymerization reaction rates. For both decomposition and polymerization reactions, a pulsed scheme was also applied, in which samples were successively heated and cooled down, under high power irradiation.

EXPERIMENTAL

Materials

2,2′-Azobis(2-methylpropionamidine) dihydrochloride (V50) and dodecyltrimethylammonium bromide (DTAB) were purchased from Sigma-Aldrich and used as initiator and emulsifier, respectively. Hydrogen peroxide (H_2O_2, 30%v/v), used as initiator, was obtained from Vetec. Analytical grade methyl methacrylate (MMA), with 100 ppm of hydroquinone, was obtained from Merck. All reagents were used directly as received, without further purification. Water was distilled and deionized by filtration through a Millipore cartridge.

Microwave reactor

The microwave reactions were conducted in a Synthos 3000 multimode microwave reactor, from Anton Paar. The microwave source was of 2.45 GHz frequency magnetron powered by a 1400 W variable power generator, which could be operated at different power levels. To prevent nonuniform heating, this instrument is equipped with a rotor system, in which eight sealed quartz vials with an 80 mL capacity can be inserted at one time. In addition, samples are stirred through a magnetic stirrer. The temperature of the sample was monitored by a gas bulb thermosensor inserted in the liquid phase of one reference vial. Additionally, an infrared sensor

placed on the rotor bottom measured the surface temperature of the vials. The microwave reactor was also equipped with a pressure transmitter, which provides pressure information of all vials. The control system supplied with the instrument enabled us to perform heating ramps with well defined sample temperature and applied power conditions programmed before the test. For the reactions performed with constant temperature, the microwave reactor was programmed to maintain constant temperature by adjusting the applied power. Consequently, after the initial heating of the reaction medium the applied power level was rather low. For the reactions with the pulsed method, on the other hand, the microwave reactor was programmed to maintain constant the power level until a given temperature was reached.

Experimental procedures

Initiator decomposition reactions under conventional heating

Initiator decomposition tests under conventional heating were carried out in aqueous media using a 1 L jacketed glass reactor, with temperature control. Deionized water (600 mL) was added into the reactor, equipped with a mechanical stirrer (150 rpm), a nitrogen inlet, a thermocouple (Type J), and a condenser to minimize the loss of reactants, especially water, through evaporation. The medium was then heated to 60, 70, or 80°C with a thermostated water bath. To remove oxygen, the medium was purged with nitrogen at a low flow-rate throughout the entire process. V50 or H_2O_2 dissolved in deionized water (40 mL) was added and the temperature was kept constant at the desired value. Samples were taken out at regular intervals of time and cooled down by immersing into an ice bath to fully stop the reaction.

Initiator decomposition reactions under microwave irradiation heating

Microwave heating–constant temperature. To perform the reactions under constant temperature, four vials were filled with aliquots (20 mL) of a previously prepared V50 or H_2O_2 aqueous solution, and purged with nitrogen during 30 min. Thereafter, the vials were closed with screw caps and were submitted to microwave irradiation during specific reaction times. The vials were promptly heated up to the reaction temperature and, after being kept at the desired temperature (60, 70, or 80°C) for a certain time interval, all the samples were collected and cooled down by immersing into an ice bath to fully stop the reaction. Sampling during the reactions was not possible because the vials with the reaction medium were

kept closed. In this way, each collected sample corresponds to an independent reaction.

The sample temperature just after the microwave heating time was determined by immersing a thermocouple into the sample directly and immediately after the prescribed reaction time. This thermocouple was similar to that one used during conventional tests. This was done in addition to the measurements obtained by the temperature sensor immersed in the reaction medium, to ensure a reliable temperature monitoring.

Microwave heating–pulsed irradiation at constant power. Pulsed microwave reactions were carried out to investigate the effect of high power microwave irradiation in V50 decomposition. After purging the 20 mL initiator solutions with nitrogen during 30 min, the samples were repeatedly heated from room temperature to 69–86°C through microwave irradiation at constant power, within short intervals of time (between 22 and 73 s depending on the applied power). The samples were cooled down in an ice bath for 4 min between microwave irradiation pulses. Experiments were carried out applying 1 to 4 irradiation pulses. After each procedure, samples were collected, cooled down, and sent for characterization. The microwave power was adjusted to be kept constant at 500 or 1400 W during sample heating.

Emulsion polymerizations under conventional heating

Polymerization reactions of methyl methacrylate under conventional heating were carried out using a 500 mL jacketed glass reactor, similar to that used in the initiator decomposition reactions. Water, monomer, and emulsifier were added into the reactor, stirred at 300 rpm and heated up to 80°C. The initiator (V50) dissolved in water was added and the temperature was kept constant. Samples were taken out at regular intervals of time and three drops of an aqueous hydroquinone solution (1 wt %) were added to fully stop the reaction. The formulations of the polymerization reactions are shown in Table I.

Emulsion polymerizations under microwave irradiation heating

The microwave-assisted polymerizations of MMA were performed using the microwave reactor Synthos 3000, with constant temperature of 80°C or with constant power of 500 and 1400 W (pulsed irradiation). The experimental procedures were similar to those used in initiator decomposition reactions, where the vials were filled with 20 mL of a previously prepared emulsion based on the formulations shown in Table I. After reaction times samples were

TABLE I
Formulations Employed in Emulsion Polymerizations of Methyl Methacrylate with Microwave and with Conventional Heating

| Formulation | Reagents (wt % related to total mass of the reaction mixture) | | | |
	V50	DTAB	MMA	Deionized water
1	0.013	0.57	20	79
2	0.005	0.57	20	79

collected and three drops of an aqueous hydroquinone solution (1 wt %) were added to fully stop the reaction

Characterization

V50 analyses

The residual concentration of V50 in decomposition reactions was determined by spectrophotometry employing a Hitachi U-1800 spectrophotometer. The absorbance of each collected sample was measured and compared to a curve prepared from standard V50 solutions, enabling one to assess the V50 concentration of the sample. The absorbance measurements were performed at 367 nm.

The decomposition reaction was assumed to follow the classical free-radical thermal initiation mechanism, where k_d is the rate constant for initiator decomposition. As the decomposition of V50 in aqueous solutions is a first order reaction, the evolution of the concentration of V50 with time can be described by eq. (1).

$$\ln \frac{[I]_{t=0}}{[I]} = k_d t \qquad (1)$$

where $[I]_{t=0}$ and $[I]$ are the molar concentrations of initiator at the beginning of the reaction and at time t, respectively.

H_2O_2 analyses

The residual concentration of H_2O_2 was determined by the classical iodometric method.[30] In this method, H_2O_2 reacts with potassium iodide in acidic solution to form iodine, which is quantified by titration with a standard solution of sodium thiosulfate. The decomposition reaction was assumed a first order reaction and the rate constant for initiator decomposition (k_d) was determined from the evolution of the concentration of H_2O_2 using eq. (1).

Polymerization samples

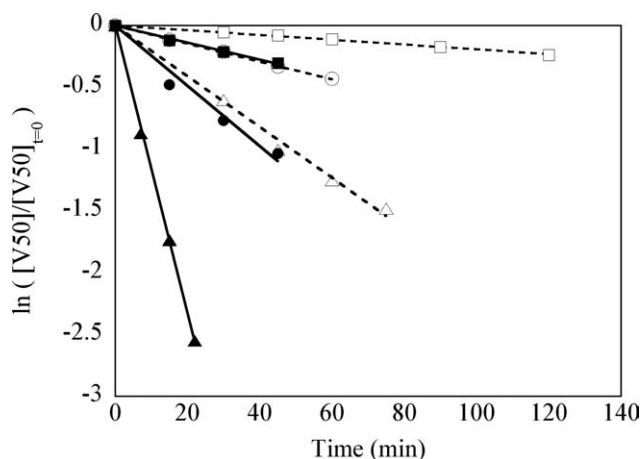Polymerization conversions were determined by gravimetry. Reaction rates were calculated fitting a

Figure 1 Variation of V50 concentration as a function of heating time. Conventional heating at (□) 60°C, (○) 70°C, and (△) 80°C. Microwave heating at (■) 60°C, (●) 70°C, (▲) 80°C (the lines represent the best fit for each condition).

polynomial to the monomer conversion curves. Average diameters of polymer particles were measured using a dynamic light scattering equipment (Zetasizer Nano S, Malvern). The number of polymeric particles was calculated from conversion and intensity average diameter results.

Determination of CMC

The critical micellar concentration (CMC) was determined by surface tension measurements. Surface tension was measured on a DCAT 11 (Dataphysics) tensiometer using the Wilhelmy plate method, at 23°C.

RESULTS AND DISCUSSION

The effect of microwave heating in V50 decomposition

The decomposition of V50 was evaluated at three different temperatures (60, 70, and 80°C) for microwave and conventional heating. All reactions were performed under constant temperature and similar experimental conditions. Figure 1 shows the variation of V50 concentration during these decomposition reactions.

It is observed in Figure 1 that microwaves promoted faster decomposition reactions, for each evaluated temperature condition. The decomposition rate constants (k_d) of V50 were calculated from the slope in Figure 1 (using eq. (1)), and are shown in Table II. The k_d values obtained from microwave heated experiments were about 3 to 5 times higher than those obtained from the conventional ones.

Similar experiments were carried out using potassium persulfate as initiator (as discussed in a previ-

ous work of this group[29]) and hydrogen peroxide (nonionic initiator). Results showed that microwaves also improved potassium persulfate decomposition reaction rates, but did not affect the hydrogen peroxide decomposition rate. Table II presents the decomposition rate constants obtained for these initiators, in reactions performed with microwave and conventional heating.

According to Table II, potassium persulfate decomposition reactions performed under microwave irradiation were about 3 to 4 times faster than reactions with conventional heating. This result agrees with that obtained for V50 decomposition. The observed microwave enhancement can be ascribed to the development of thermal gradients within the sample. The thermally induced decomposition of both V50 and potassium persulfate initiators generate ionic radicals, which may contribute to microwave heating through ionic conduction mechanism. Electromagnetic radiation induces ions migration, leading to rapid local temperature enhancements. The originated hot spots cannot be detected because local temperature measurements are not accessible, and we can only measure the bulk temperature.

The decomposition rate constants of hydrogen peroxide, on the other hand, were similar under both heating conditions. As the radicals formed throughout hydrogen peroxide decomposition are nonionic, and considering the inexistence of another ion in the solution, the dielectric heating on this medium is a consequence of only dipole rotations, and ionic conduction mechanism is restricted. Therefore, the development of hot spots is not favored, and microwave effects are insignificant in the system. Table III shows the radicals formed from the decomposition of the three initiators presented.

TABLE II
Decomposition Rate Constants (k_d) of V50 (obtained experimentally), Potassium Persulfate (KPS, obtained from literature) and Hydrogen Peroxide (H$_2$O$_2$, obtained experimentally), for Microwave (MW) and Conventional Heating (CH)

Initiator	T (°C)	k_d (s^{-1}) Microwave	k_d (s^{-1}) Conventional	k_d MW/ k_d CH
V50[a]	60	1.00×10^{-4}	3.21×10^{-5}	3.12
V50[a]	70	4.48×10^{-4}	1.21×10^{-4}	3.70
V50[a]	80	1.93×10^{-3}	3.42×10^{-4}	5.64
KPS[b]	60	2.97×10^{-5}	1.00×10^{-5}	2.97
KPS[b]	70	1.03×10^{-4}	2.83×10^{-5}	3.64
KPS[b]	75	1.86×10^{-4}	4.25×10^{-5}	4.38
KPS[b]	80	3.31×10^{-4}	1.02×10^{-4}	3.24
H$_2$O$_2$[a]	80	1.17×10^{-5}	1.00×10^{-5}	1.17

[a] Experimental data.
[b] Ref. 29.

TABLE III
Radicals Formed from the Decomposition of Initiators
V50, H_2O_2, and KPS

Initiator	Radical
V50	(structure)
H_2O_2	$HO^\bullet$
KPS	$SO_4^{\bullet-}$

To study the effect of the microwave power level on V50 decomposition, reactions under high power irradiation were performed. In such reactions, heating and cooling cycles were carried out, submitting the samples to irradiation pulses at constant power during short intervals of time, with subsequent cooling in an ice bath for 4 min. These reactions were performed with constant power of 500 or 1400 W. Power profiles for pulsed irradiation reactions at constant power and for reactions performed at constant temperature are shown in Figure 2.

Figure 2 shows that power is alternately on and off in pulsed reactions, whereas in reactions at constant temperature, it is continuously on, remaining at low levels for almost the entire experiment (except in the first seconds, when power has its maximum value to heat the sample up to the desired temperature). This procedure with cycles of heating and cooling allows one to supply a greater amount of energy to the reaction media compared to those tests conducted at constant temperature. The total energy applied as a function of the irradiation time is shown in Figure 3, for reactions at constant temperature and at constant power. The total energy was calculated by the numerical integration of the power profiles shown in Figure 2. It is observed that
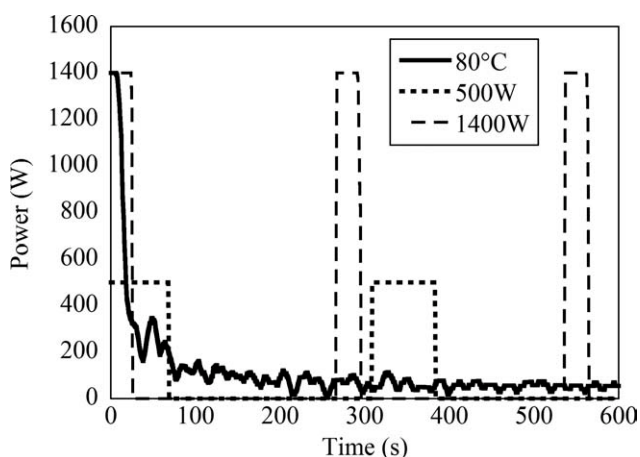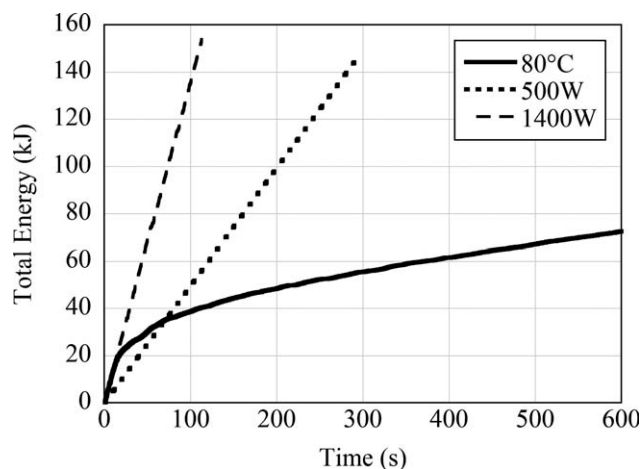

Figure 3 Total energy applied with irradiation time for microwave heating at constant temperature (80°C) and at constant power (500 and 1400 W).

60 kJ were obtained with 44 s of 1400 W microwave irradiation, or 121 s of 500 W microwave irradiation, or even 373 s of variable power microwave irradiation, adjusted to keep constant temperature (80°C).

In addition, in the pulsed irradiation method, the temperature of the samples is continuously increased and decreased, preventing sample overheating. Figure 4 presents the temperature profiles of reactions performed at constant temperature and at constant power.

Figure 5 shows the V50 decomposition percentages, obtained in reactions performed with heating and cooling cycles. In these reactions, the samples were heated at constant 500 or 1400 W until the final temperature (83 ± 3 or 71 ± 2°C) was achieved. The cycles were subsequently repeated, resulting in the increment of total energy. Decomposition percentages were computed from eq. (2).
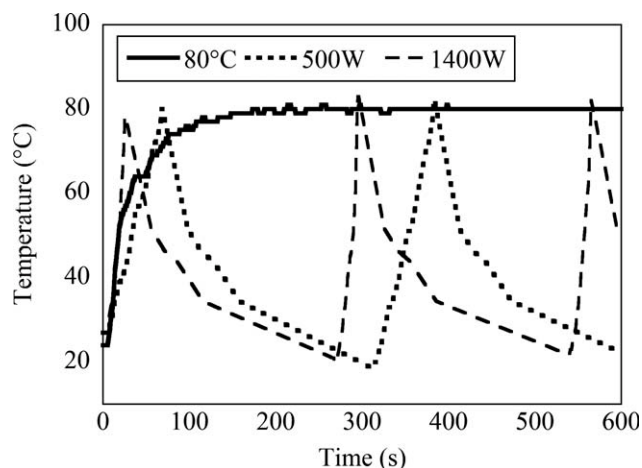

Figure 2 Power profiles for microwave heated reactions: constant temperature (80°C) and pulsed irradiation at constant power (500 and 1400 W).

Figure 4 Temperature profile for microwave heated reactions: constant temperature (80°C) and pulsed irradiation at constant power (500 and 1400 W).
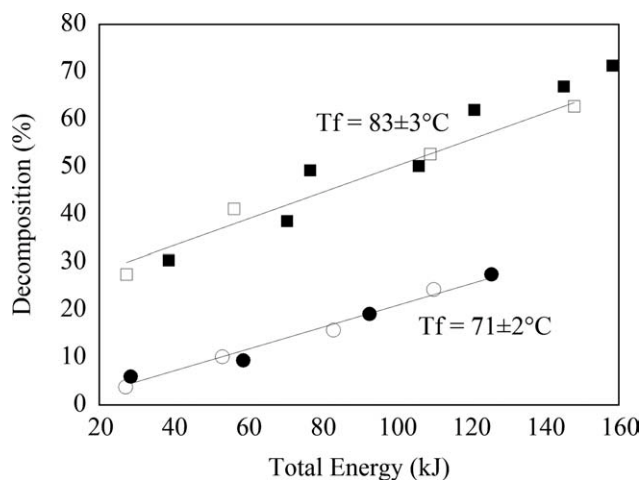
Figure 5 V50 decomposition as a function of the total energy applied. Final temperatures of 83 ± 3°C at (□) 500 W, (■) 1400 W, and 71 ± 2°C at (○) 500 W, (●) 1400 W (the lines represent the best fit for each final temperature condition).

$$\text{Decomposition (\%)} = \frac{[\text{V50}]_{t=0} - [\text{V50}]}{[\text{V50}]_{t=0}} \times 100 \quad (2)$$

It is observed in Figure 5 that the decomposition of V50 was not affected by the power level. Both 500 and 1400 W power irradiation conditions resulted in the same yield. The decomposition percentages seem to be dependent on total energy applied and final temperature of the solution. Moreover, these decompositions were achieved in short irradiation times, showing that faster reactions can be performed with this method. Table IV presents the total irradiation time for reactions conducted under different power levels. The reduction of time is evident, if we compare reactions at 500 and 1400 W. To achieve 83°C, it was necessary about 73 s of microwave irradiation at 500 W, but only about 28 s at 1400 W. Thus it is possible to reduce dramatically reaction time by applying high power irradiation, without changing the provided amount of energy.

A comparison between the two heating methods (constant temperature or pulsed irradiation at constant power) is presented in Figure 6. As one can observe, similar decomposition profiles were obtained for both methods, where the decomposition
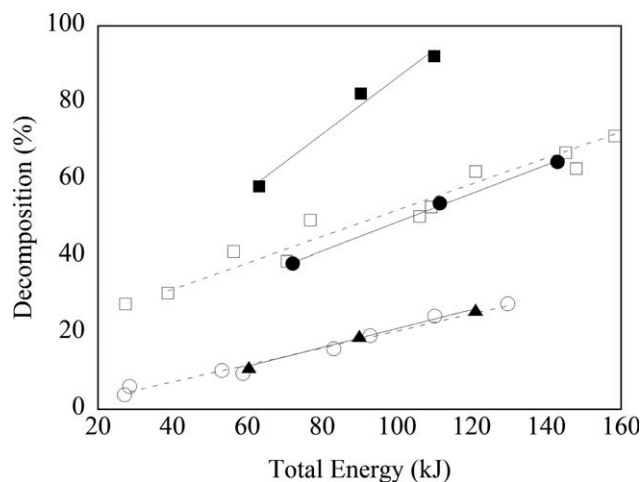
TABLE IV
Average Irradiation Time Applied to Achieve 83 ± 3°C or 71 ± 2°C, Under Constant Power (500 or 1400 W)

Temperature (°C)	Power (W)	Average irradiation time (s)	Power (W)	Average irradiation time (s)
83 ± 3	500	73	1400	28
71 ± 2	500	59	1400	22

Figure 6 V50 decomposition as a function of the total energy applied with temperature kept constant at (▲) 60°C, (●) 70°C, and (■) 80°C; with power kept constant to achieve final temperatures of (○) $T_f = 71 \pm 2$°C and (□) $T_f = 83 \pm 3$°C (the lines represent the best fit for each condition).

percentage increases with the total energy and the temperature.

Considering the results shown in Figure 6, we can state that the V50 decomposition percentages obtained in microwave-assisted reactions depend on the total energy applied, the final (or constant) temperature of the solution and the heating method employed.

The effect of microwave heating on emulsion polymerization reactions

Emulsion polymerization reactions of methyl methacrylate were performed with two different initiator concentrations, according to formulations shown in Table I. Figures 7–9 show the evolution of conversion, reaction rate (R_p) and average particle diameter (D_p) during these reactions under conventional and microwave heating. In Figures 7 and 8, it is observed that microwave heating resulted in faster reactions for the two studied formulations (with 0.013 and 0.005 wt % of initiator V50). The size of the particles formed during microwave heated reactions was similar to that obtained during the conventional polymerizations, as shown in Figure 9. These results show that the observed enhancements in initiator decomposition reaction rates under microwave irradiation presented above can affect the polymerization reaction rates, but for this system have no considerable effect on the diameter of polymeric particles. This can possibly be ascribed to the low emulsifier concentration used in these polymerization reactions. The concentration of DTAB was only 1.86 times greater than the measured CMC (12.6 mM) for this emulsifier. In this way, the reduced
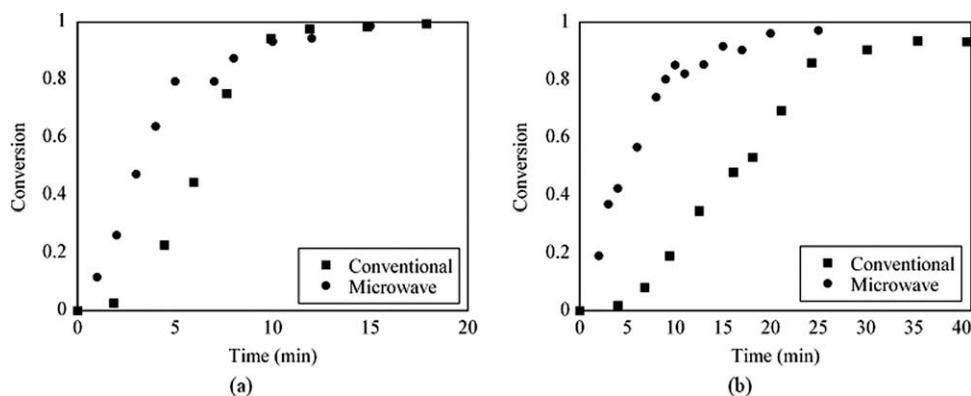
Figure 7 Evolution of conversion during MMA emulsion polymerizations with microwave and conventional heating at constant temperature 80°C: (a) formulation 1 (0.013 wt % of V50); (b) formulation 2 (0.005 wt % of V50).

concentration of emulsifier may hamper the increase of the number of stable particles in these reactions with microwave enhanced initiator decomposition. For systems using an anionic initiator in which a microwave effect was observed on the nucleation stage,[23] leading to lower particle diameters and, consequently, to a higher number of polymeric particles in microwave reactions, the concentration of emulsifiers was much greater (eight times higher) than the CMC value (0.10 mM).

Polymerization reactions were also carried out using cycles of heating and cooling, with constant power irradiation of 500 or 1400 W. Figure 10 shows the evolution of conversion in reactions with constant power using formulation 1 (0.013 wt % of initiator V50). Rapid reactions were obtained using the method of cycles. Conversions of about 90% were achieved applying seven cycles (about 31 s of microwave irradiation of 1400 W or 68 s of microwave irradiation of 500 W) whereas in reactions with constant temperature, it was necessary 10 min of microwave irradiation to achieve similar conversion. It is observed in Figure 10 that the power level did not affect the monomer conversion.

CONCLUSIONS

The decomposition of initiator V50 was improved by microwave irradiation, comparing with conventional heating method. The decomposition rate constants determined for microwave-assisted reactions were about 3 to 5 times higher than those obtained for conventional ones. This result was ascribed to the presence of ions – the formed radicals – in the solution that provide specific heating by ionic conduction mechanism under microwaves. The same behavior had been observed for potassium persulfate decomposition reactions performed under microwave irradiation.[29] These were about 3 to 4 times faster than reactions with conventional heating. The decomposition rate constants of hydrogen peroxide, on the other hand, were similar under both heating conditions, as the radicals formed are nonionic.

The use of high power microwave irradiation allowed applying a great amount of energy in short time intervals, promoting rapid decomposition reactions. Despite the time saving, the power level did not affect the obtained decomposition amount,
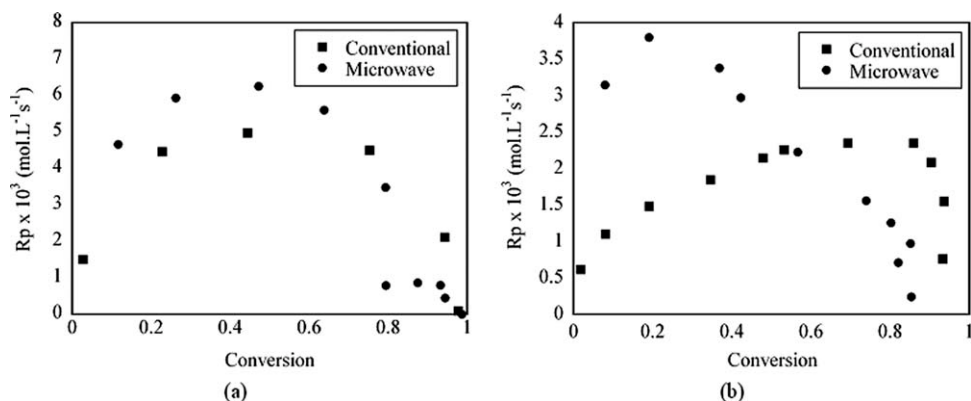

Figure 8 Evolution of reaction rate (R_p) during MMA emulsion polymerizations with microwave and conventional heating at constant temperature 80°C: (a) formulation 1 (0.013 wt % of V50); (b) formulation 2 (0.005 wt % of V50).
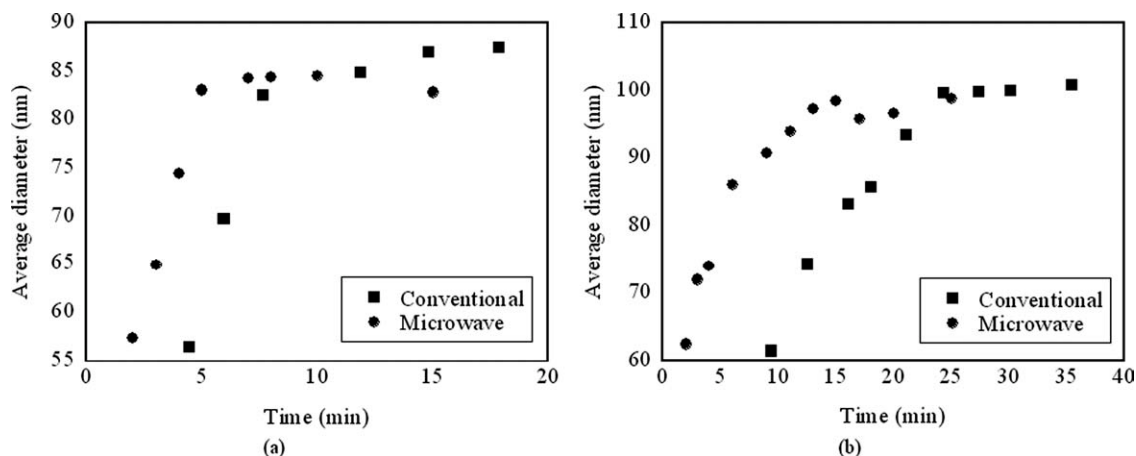
Figure 9 Evolution of average diameter of polymeric particles (D_p) during MMA emulsion polymerizations with microwave and conventional heating at constant temperature 80°C: (a) formulation 1 (0.013 wt % of V50); (b) formulation 2 (0.005 wt % of V50).

considering decomposition as a function of total energy. Besides of depending on total applied energy, the decomposition percentage was a function of final temperature.

Emulsion polymerization reactions of MMA were faster under microwave irradiation, compared with the conventional heated ones. This acceleration can be linked to the observed enhancements in initiator decomposition rates promoted by microwaves. Using high power microwave irradiation rapid polymerizations were obtained achieving high conversions within short intervals of irradiation.

The microwave effects observed in this work show the advantages of this heating method in the decomposition reaction of V50. This fundamental kinetic study may contribute to the development of

polymerization processes focusing on a better use of energy or aiming materials with different properties.

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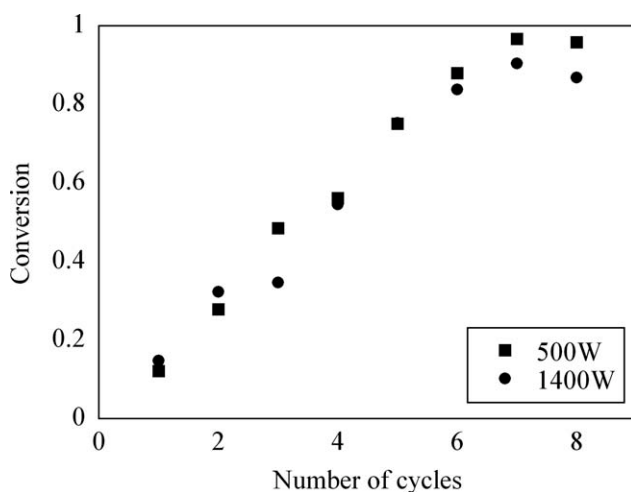
Figure 10 Evolution of conversion during MMA emulsion polymerizations with cycles of cooling and heating, with constant power of 500 or 1400 W, using formulation 1 (0.013 wt % of V50).

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