Ionic Liquid as Surfactant in Microwave-Assisted Emulsion Polymerization

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ABSTRACT: The aim of this work is to study the use of an ionic liquid (IL) as surfactant in emulsion polymerization reactions and to evaluate its effect when these reactions are heated under microwave irradiation. The IL 1-n-dodecyl-3-methylimidazolium chloride was chosen to replace the surfactant dodecyltrimethylammonium bromide (DTAB) in methyl methacrylate emulsion polymerizations. The conversion evolutions and the final average diameter of polymeric particles were quite similar for reactions using the surfactant DTAB or the IL, showing that the IL acted efficiently as surfactant in emulsion polymerizations. Comparing the polymerization reactions performed under microwave irradiation and conventional heating, reaction rate enhancements were obtained for both DTAB and IL. Using a pulsed scheme, under high-power microwave irradiation, slightly higher reaction rates and molecular weights were obtained in reactions using IL, in comparison with surfactant DTAB, indicating the existence of some specific effects linked to IL–microwaves interaction. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Ionic liquids (ILs) constitute a new generation of solvents that have attracted wide interest as reaction media and as substitutes for conventional volatile organic solvents in numerous applications. Most ILs consist of organic cations combined with anions of organic or inorganic nature. Changes of the functional groups of the cation or the anion allow ILs to be used as tailor-made solvents, electrolytes, surfactants, and reagents in organic synthesis and homogeneous catalysis.[1,2] Besides possessing interesting dielectric properties, the ILs can be designed to achieve specific melting point, viscosity, density, and hydrophobicity, making these species very attractive for both microwave and conventional processes.[3] The advantage of using microwave irradiation, compared with conventional processes, is that it usually reduces reaction time by efficient heating, making easy the path to high-temperature reactions. Second, microwave heating is also known to suppress side reactions, increase yields, and improve purity and reproducibility.[4,5]

The use of ILs as solvents in organic synthesis conducted by microwave irradiation is justified by its high capacity to absorb microwaves and to convert electromagnetic energy into heat. ILs have been generally viewed as species that interact very efficiently with microwaves through the ionic conduction mechanism and are quickly heated at rates easily exceeding 10°C/s without any considerable pressure increase.[3,6] In this way, some organic compounds can be heated up to 200°C within 20 s in the presence of ILs under microwave irradiation.[6–8]

Polymerization reactions using ILs and microwave heating have been extensively studied.[3,7–11] Most of these reactions use ILs as solvents in homogeneous polymerizations, showing faster heating and lower reaction times in the presence of microwaves. Among the main ILs used in these investigations, imidazolium cation-based ILs are by far the most popular, because they are easy to modify, stable under acidic conditions, and have low charge density that enables one to construct low-melting salts from them.
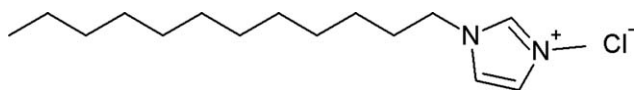
Scheme 1. Molecular structure of the ionic liquid [C$_{12}$mim]Cl.

Another interesting feature achieved by imidazolium-based ILs relates with the amphiphilic nature of *n*-alkylimidazolium cations. These species possess interfacial and aggregation behaviors in aqueous solutions, leading to the formation of micelles.[2,12] Changes in the alkyl chain length or in the type and size of the anion used can affect the structure and dynamics of micellar aggregates formed, leading to changes in critical micellar concentration (CMC).[12–16] Therefore, these ILs have similar behavior of surfactants in aqueous solutions, making them very interesting for heterogeneous polymerization purposes.
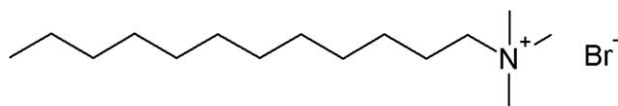
In suspension polymerization, ILs can act as stabilizer agents, inducing electrostatic charges on the surface of the monomer droplets and polymer particles to prevent coalescence. Guerrero-Sanchez et al.[17] studied the suspension polymerization of styrene using ILs as stabilizers and obtained polymer beads with specific characteristics, depending on the type and concentration of the IL used. In another work, Yan and Texter[18] produced polymeric nanoparticles by microemulsion polymerization, using an oil-soluble initiator and the IL 1-*n*-dodecyl-3-methylimidazolium bromide. It is worth mentioning that both studies related above were conducted using conventional heating.

A recent study from our group has shown that a set of ILs can be successfully applied as surfactant during emulsion polymerization reactions conducted under microwave irradiation.[7] This article presents this new application of ILs based on the surfactant action of 1-*n*-dodecyl-3-methylimidazolium chloride ([C$_{12}$mim]Cl) during microwave-assisted emulsion polymerization reactions.

EXPERIMENTAL

Materials
A series of methyl methacrylate (MMA, >99%; Merck, Germany) microwave-assisted emulsion polymerization reactions were carried out at different IL concentrations using 2,2′-azobis(2-methylpropionamidine)dihydrochloride (V50, >98%; Sigma-Aldrich, USA) as initiator. The IL used in this work was [C$_{12}$mim]Cl. Tests with dodecyltrimethylammonium bromide (DTAB, >99%; Sigma-Aldrich, USA) as cationic surfactant were also performed for comparison, because of the similarity between the molecular structures of [C$_{12}$mim]Cl and DTAB (Schemes 1 and 2). Distilled water was used as continuous medium. All reagents were used directly as received, without further purification. The synthesis of the IL ([C$_{12}$mim]Cl) was based on the metathesis route for the formation of imidazolium

Table I. Formulations of the Polymerization Reactions

Reaction	Reagents (wt % related to total mass of the reaction mixture)				
	[C$_{12}$mim]Cl	DTAB	V50	MMA	Water
IL-1	1.29[a]	–	0.013	20	79
IL-2	0.66[b]	–	0.013	20	79
IL-3	0.33[c]	–	0.013	20	79
DTAB-1	–	0.57[d]	0.013	20	79

[a]3.4 × CMC., [b]1.7 × CMC., [c]0.8 × CMC., [d]1.8 × CMC (related to aqueous phase).

halides, in accordance to the procedures of synthesis and purification described elsewhere.[19] The general procedure for synthesis and purification carried out in this work yielded ILs with high purity (>98%).

Microwave Reactor
The microwave reactions were conducted in a Synthos 3000 multimode microwave reactor, from Anton Paar, with a microwave source of 2.45 GHz, in accordance with the procedures described by previous works of this group.[20–22] This instrument is equipped with a rotor system and a magnetic stirrer, preventing nonuniform heating of the samples. A gas bulb thermosensor inserted in the liquid phase of one reference vial was used to monitor the temperature of the samples. In addition, the microwave reactor was equipped with a pressure transmitter, which provides pressure information of all vials, and also an infrared sensor placed on the rotor bottom to measure the surface temperature of the vials. This reactor is powered by a 1400-W variable power generator, which could be operated at different power levels to perform heating ramps with well-defined sample temperature. The control system enables us to program the temperature and power conditions prior to the test. Therefore, reactions with constant temperature were
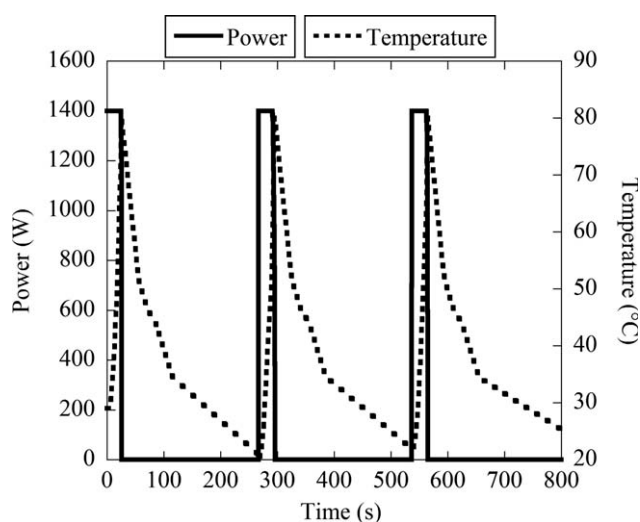

Scheme 2. Molecular structure of the surfactant DTAB.

Figure 1. Schematic representation of power and temperature profiles in pulsed microwave reactions (cycles of heating and cooling under high-power irradiation).
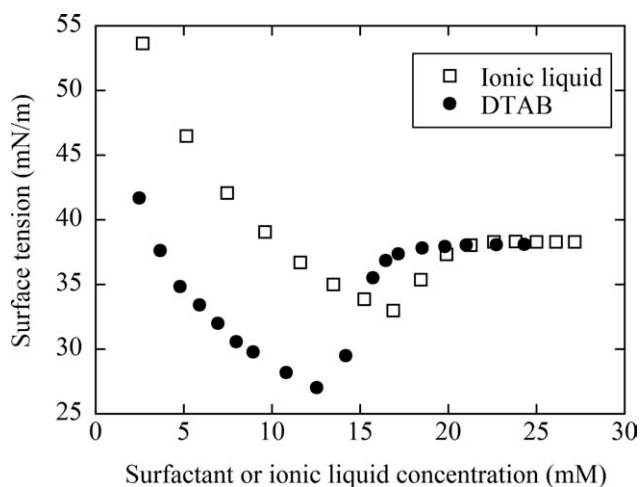
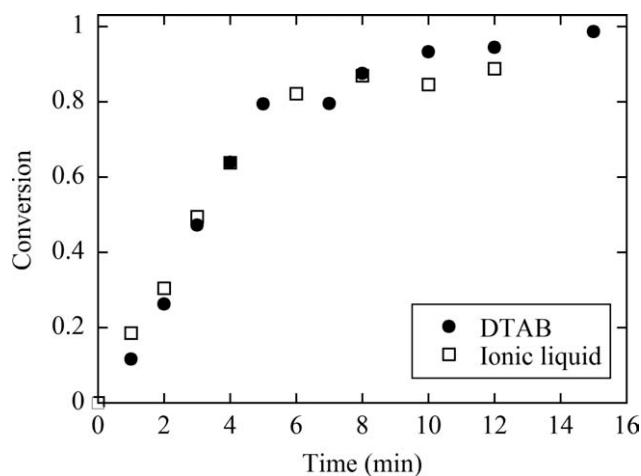**Figure 2.** Variation of the surface tension with the concentration of DTAB and ionic liquid aqueous solutions.

Figure 3. Evolution of conversion in microwave-assisted emulsion polymerizations using either surfactant DTAB or ionic liquid (IL-2).

performed by adjusting the applied power. On the other hand, the pulsed method consisted of keeping the power level constant, until a given temperature was reached.

Polymerization Reactions

Initially, emulsion polymerization reactions were performed under constant temperature (80°C). For this purpose, the microwave reactor was programmed to maintain constant temperature by adjusting the applied power. To proceed with the polymerizations, the reactor vials were filled with 20 mL of a previously prepared emulsion (based on the formulations shown in Table I) and purged with nitrogen for 30 min to remove the oxygen. After purging, the vials were closed and submitted to microwave irradiation during specific reaction times. During these reactions, the vials were promptly heated up to the reaction temperature and being kept at 80°C for a certain time interval. Thereafter, the samples were collected and three drops of an aqueous hydroquinone solution (1 wt %) were added 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 pulsed method was used to investigate the effect of high-power microwave irradiation in emulsion polymerizations. To proceed with pulsed microwave reactions, the vials filled with

20 mL of the previously prepared emulsion (formulations shown in Table I) and purged with nitrogen were repeatedly heated from room temperature to 80°C through microwave irradiation at constant power (1400 W) within short intervals of time (see Figure 1). Each microwave irradiation pulse was of about 30 s, which was just the time needed to heat the reaction medium from room temperature to 80°C. After each pulse, the samples were cooled down in an ice bath for 4 min. In these experiments, one to eight irradiation pulses were applied. Thereafter, samples were collected, and three drops of an aqueous hydroquinone solution (1 wt %) were added to fully stop the reaction.

To evaluate the microwave effects in the emulsion polymerization reactions with ILs, conventional heated reactions were carried out using a 500-mL jacketed glass reactor, equipped with a mechanical stirrer, a nitrogen inlet, a thermocouple (Type J), and a condenser, in accordance with procedures described in a
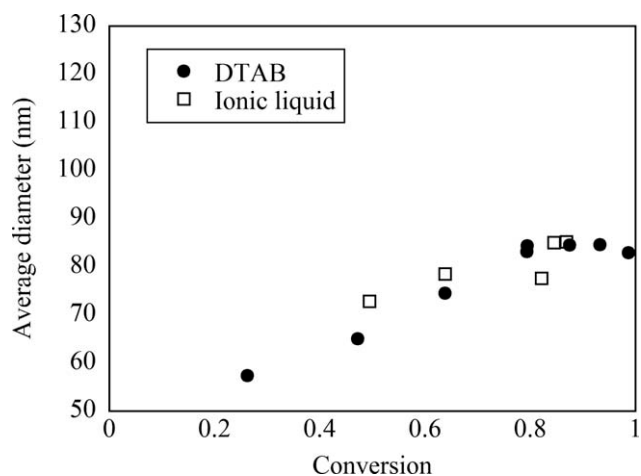
Table II. Critical Micellar Concentration (CMC) for Surfactant DTAB and Ionic Liquid [C_{12}mim]Cl Determined Experimentally and Obtained from Literature (at Room Temperature)

Compound	CMC (mM)	Reference
[C_{12}mim]Cl	16.7	This work
	15	Blesic et al.[14]
	14	Bai et al.[23]
	13.17	El Seoud et al.[33]
DTAB	12.6	This work
	11.6 to 13	Lin and Lin[34]

Figure 4. Evolution of average diameters of the polymeric particles in microwave-assisted emulsion polymerizations using either surfactant DTAB or ionic liquid (IL-2).
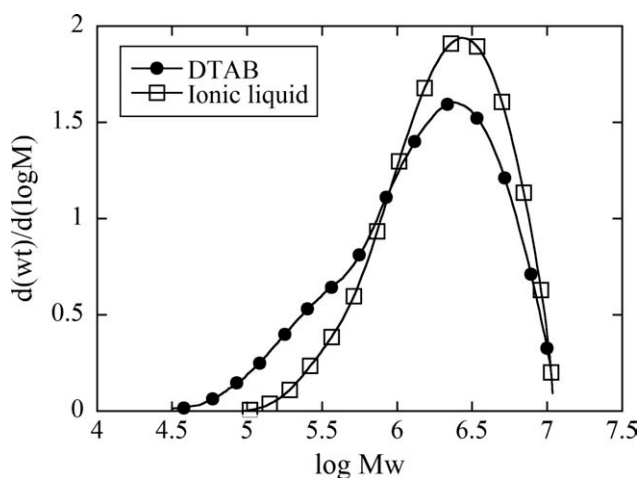
Figure 5. Molecular weight distributions of the polymers obtained in microwave-assisted emulsion polymerizations using either surfactant DTAB or ionic liquid (IL-2).

previous work.[21] Water, monomer, and IL (or surfactant) were added into the reactor, stirred at 300 rpm, and heated up to 80°C. The medium was purged with nitrogen at a low flow rate throughout the entire process. The initiator (V50) dissolved in water was added, and the temperature was kept constant. Samples were taken 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 were the same for both heating methods (Table I).

Characterization

Monomer conversions were calculated from the ratio of polymer weight and initial monomer weight. The polymer weight of each sample was determined by gravimetry. Intensity-average diameters of polymer particles were measured using the dynamic light scattering equipment Zetasizer Nano S (from Malvern). For this analysis, latex samples were diluted to 1 : 15
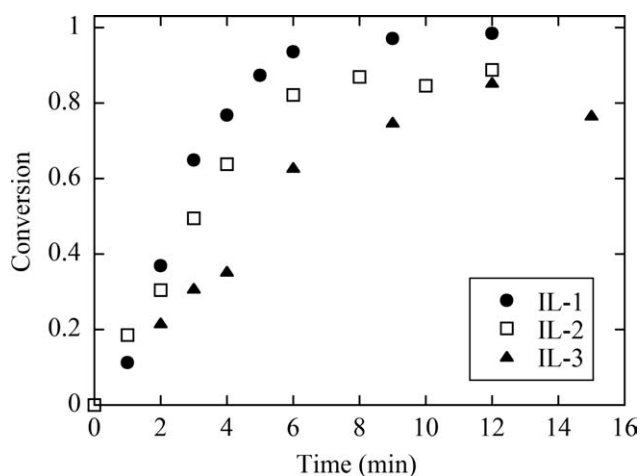

Figure 6. Evolution of conversion in microwave-assisted emulsion polymerizations using different concentrations of ionic liquid (reactions IL-1, IL-2, and IL-3).
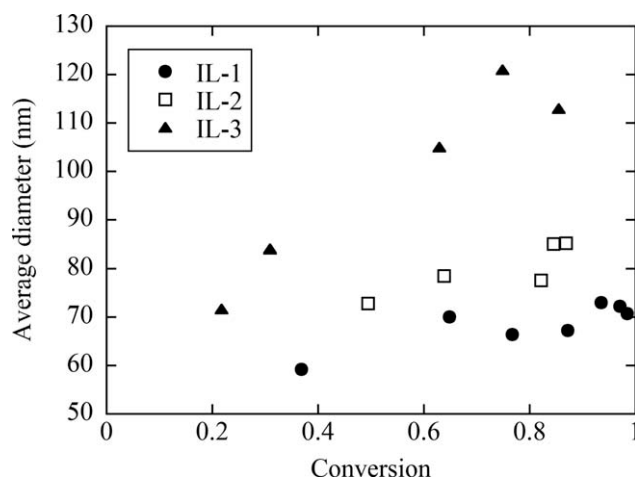

Figure 7. Evolution of average diameters of polymeric particles in microwave-assisted emulsion polymerizations using different concentrations of ionic liquid (reactions IL-1, IL-2, and IL-3).

with distilled water. Molecular weight distributions of the obtained polymers were determined by gas permeation chromatography using a Shimadzu Chromatograph (RID detector), and three columns Shim-Pack GPC-800 Series (GPC-801, GPC 804, and GPC 807), from Shimadzu, in series. Tetrahydrofuran was used as eluent (flow rate 1.0 mL/min at 35°C), and calibration was done using polystyrene standards ($M_w = 580$ to 9.22×10^6).

Critical Micellar Concentration

Surface tension measurements were conducted to determine the CMC of both the surfactant DTAB and the IL [C_{12}mim]Cl in aqueous solutions. The surface tensions were determined by the Wilhelmy plate method, using the tensiometer DCAT11 (Dataphysics), at 23°C.

RESULTS AND DISCUSSION

According to the results shown in Figure 2, the variation of the surface tension with the concentration of IL aqueous solutions presented similar profile to that obtained when DTAB aqueous solutions were used. This indicates the capacity of the IL to form micelles and the possibility of its use as surfactant. The CMCs determined for both compounds were in the same range of values and also very similar to the values reported in literature, as shown in Table II.

Results of polymerization reactions under microwave irradiation using DTAB or IL as surfactant (which corresponds to reactions

Table III. Ionic Liquid Concentration and Number of Polymeric Particles (Per Liter of Reaction Medium) Obtained in Reactions IL-1, IL-2, and IL-3

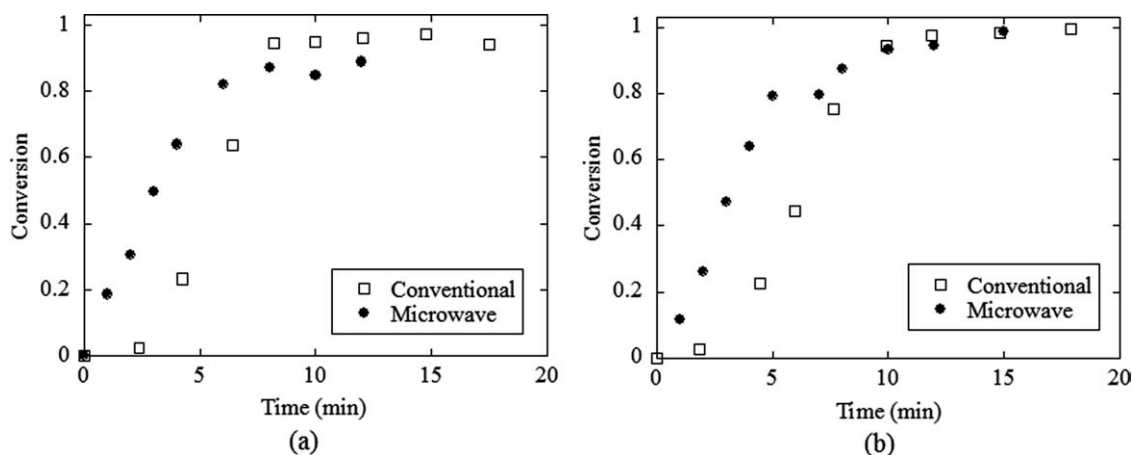| Reaction	[C_{12}mim]Cl (wt %)	Np (particles per liter)
IL-1	1.29	8.1×10^7
IL-2	0.66	4.5×10^7
IL-3	0.33	1.6×10^7

Figure 8. Evolution of conversion in emulsion polymerizations with microwave or conventional heating using (a) ionic liquid (IL-2) and (b) surfactant DTAB.

DTAB-1 and IL-2, respectively) are shown in Figures 3–5. It can be seen that the conversion evolutions were practically equal. In addition, very small differences were obtained in the average diameter of polymeric particles during the reactions, resulting in final particle diameters quite similar for both reactions. These results demonstrate not only the stabilization of particles by the IL as well as by the surfactant DTAB but also that the IL allows particle formation by micellar nucleation as in these reactions IL and DTAB concentrations were above the respective CMCs, as shown in Table I. Furthermore, the micellar aggregation number for the IL used in this work is smaller than that for DTAB. The values reported in literature are N_{agg} = 37 for [C$_{12}$mim]Cl[23] and N_{agg} = 55 for DTAB.[24] Thus, the total number of micelles available for particle nucleation via the micellar nucleation mechanism was higher in the reaction using IL than in the reaction using the surfactant DTAB. Molecular weights of polymers obtained using IL were slightly higher than those obtained with surfactant DTAB (see Figure 5). However, this little difference alone cannot support the existence of some spe-

cific effect of the IL in reactions conducted under microwave irradiation with constant temperature.

The evolution of conversion when the concentration of IL was varied in the microwave-assisted emulsion polymerization reactions is shown in Figure 6. The reaction rates were higher for the reaction with higher IL concentration (which corresponds to reaction IL-1). This behavior is also observed in conventional reactions using surfactant DTAB.[25] It is also observed in Figure 6 that even for IL concentrations below the CMC (reaction IL-3), 85% of MMA conversion was obtained. This result for reaction IL-3 indicates that the IL was able to stabilize particles nucleated from the aqueous phase (homogeneous nucleation), yielding polymeric particles with average diameters around 115 nm (Figure 7). In addition, average particle sizes decrease with the increase of the IL concentration, in the same way as expected for common surfactants.

The number of polymeric particles (Np) obtained at the end of these reactions can be calculated from average diameter and
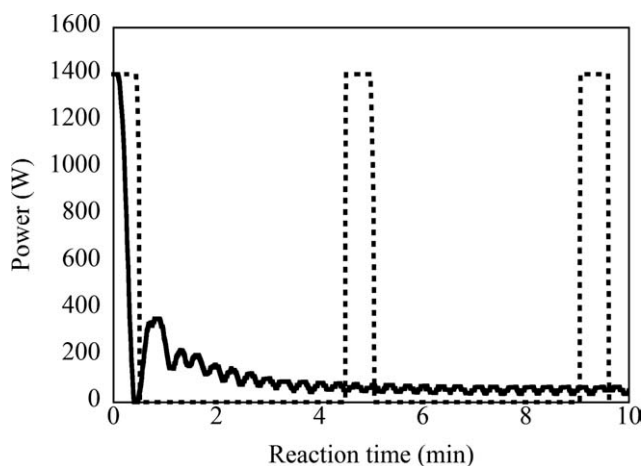

Figure 9. Schematic representation of power profiles in microwave reactions with constant temperature (continuous line) or with cycles of heating and cooling under high-power irradiation (dashed line).
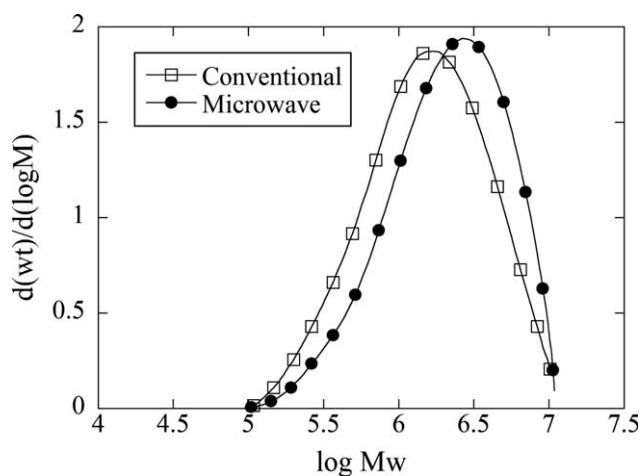

Figure 10. Molecular weight distributions of the polymers obtained in emulsion polymerizations with microwave or conventional heating using ionic liquid (IL-2).
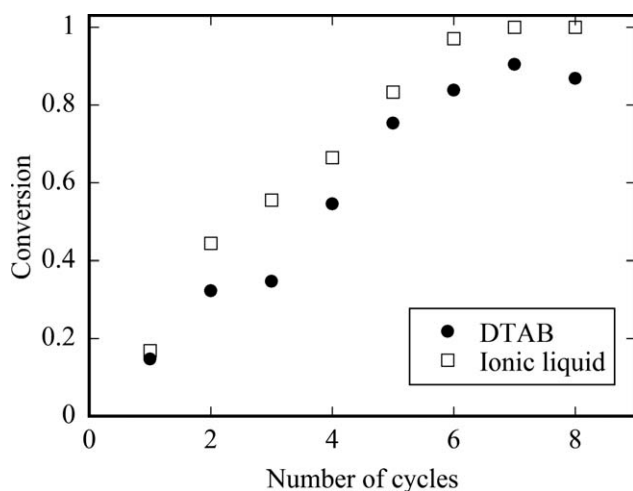
Figure 11. Evolution of conversion in emulsion polymerizations with cycles of heating and cooling under microwave irradiation using either ionic liquid (IL-2) or surfactant DTAB.

Figure 13. Evolution of average diameters of polymer particles obtained in emulsion polymerizations with cycles of heating and cooling under microwave irradiation using either ionic liquid (IL-2) or surfactant DTAB.

conversion data. Final Np calculated for reactions IL-1, IL-2, and IL-3 (see Table III) showed that Np increases with the concentration of IL. In a fundamental study, Feeney et al.[26] showed that the dependence of Np on the surfactant (sodium dodecyl sulfate) concentration, [S], for the formation of polymer particles in emulsion polymerizations with surfactant concentrations at or above the CMC, is described by the following equation:

$$Np \propto [S]^{0.4-1.2} \qquad (1)$$

They observed that the exponent of [S] decreases from 1.2 to 0.4 with the increase of [S]. When compared with our results, it can be seen that the dependence of Np on [IL] is in accordance with that predicted for common surfactants.
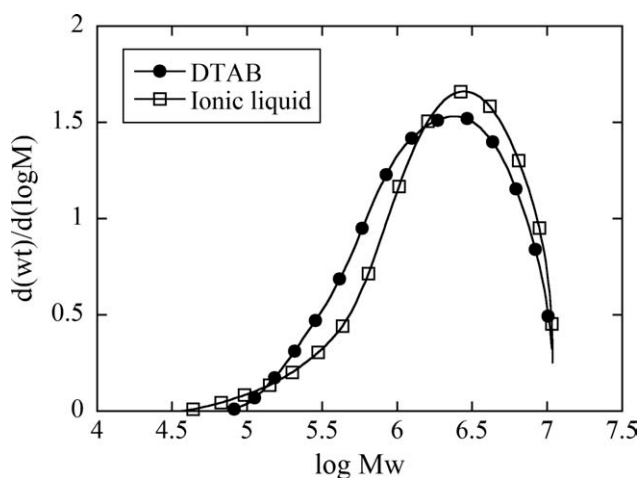

Figure 12. Molecular weight distributions of the polymers obtained in emulsion polymerizations with cycles of heating and cooling under microwave irradiation using either ionic liquid (IL-2) or surfactant DTAB.
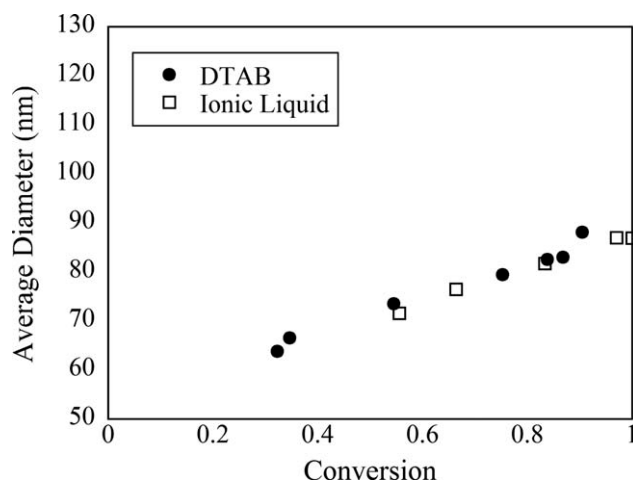
To verify if the IL [C$_{12}$mim]Cl used in our work enhances the reaction rate of MMA emulsion polymerizations conducted under microwave irradiation, the evolution of conversion for microwave-heated reactions and that performed under conventional heating is compared [Figure 8(a)], using IL as surfactant (which corresponds to reaction IL-2). It was observed that faster reactions were obtained using microwave irradiation. However, this result cannot be seen as a particular effect attributed to the IL or to specific microwaves–IL interactions as claimed in the literature,[27] as the microwave acceleration has been observed in several emulsion polymerization reactions using common surfactants.[20,21,28–30] As observed in Figure 8(b), which presents the evolution of conversion for microwave and conventional heated reactions using DTAB, the same reaction rate enhancement is seen when using microwaves. This acceleration has already been attributed to increases in initiator decomposition rates promoted by microwaves.[21] Because microwave heating is a consequence of the movement of ions or molecule dipoles caused by the electric field of the incident radiation, the polarity of molecules and the presence of ions in a substance determine its capacity to transform electromagnetic energy into heat. This heating effect is well known from the microwave literature[31,32] and can be described mathematically through the so-called dielectric heating equation:

$$p = 2 \cdot \pi \cdot f \cdot \varepsilon_0 \cdot \varepsilon'' \cdot E^2 = \sigma \cdot E^2, \qquad (2)$$

where the power dissipated per unit volume (p) is related to the permittivity of free space (ε_0), the loss factor (ε''), the electric field intensity (E), and its frequency (f). Because the electrical conductivity (σ) effects are usually included within the loss factor, it is clear from this equation that the power dissipation is proportional to the electrical conductivity. In this sense, the conductivity values of aqueous solutions containing DTAB or [C$_{12}$mim]Cl measured at the same conditions (70°C and 18.5 mM) correspond to $\sigma_{DTAB} = 1736$ μS/cm and $\sigma_{IL} = 2568$ μS/cm. As a consequence, the greater conductivity of the IL would

explain the greater power dissipation per unit volume of the sample and thus the heating effect. This point may be crucial for those experiments involving high-power irradiation. However, for reactions under controlled temperature (as in the case of Figure 8), this heating effect must be masked because the greater the conductivity of the sample, the lower the energy that might be applied to the sample reach the set-point temperature. Figure 9 shows the difference in the power profile between experiments carried out under high-power irradiation and that with constant temperature. In reactions with constant temperature, the applied power is high in the first seconds in order to heat the sample up to the desired temperature, and then decreases to low values, remaining at low levels along the reaction.

Despite the acceleration in the reaction rate, microwave heating also promoted an increase of the molecular weight of polymers obtained using IL, when compared with conventional heating, as presented in Figure 10. This result makes the microwave heating even more attractive for polymerization reactions, as, in general, under conventional heating, faster polymerization reactions result in polymers with lower molecular weights.

Emulsion polymerizations with cycles of heating and cooling under microwave irradiation (schematically shown in Figure 1) were performed to evaluate the effect of high-power irradiation (1400 W) on reactions using the IL and to compare with reactions using the surfactant DTAB. Figure 11 shows the evolution of conversion for these reactions. It is observed that for both surfactant and IL, reactions were fast and final conversions were obtained by applying only seven cycles of heating and cooling (about 30 s each microwave irradiation pulse). Higher conversions were obtained in the reaction using the IL. This effect was not observed in reactions with constant temperature, indicating an advantage of using ILs under high-power microwave irradiation.

Molecular weight distributions of the polymers obtained in emulsion polymerization reactions under microwave irradiation with constant power are shown in Figure 12. A slight increase in the molecular weight was also observed for reactions using IL.

The average particle diameter profiles during emulsion polymerizations with cycles of heating and cooling under microwave irradiation using IL or surfactant DTAB were virtually the same, as shown in Figure 13. These results indicate that the higher reaction rate of the reaction using IL under high-power irradiation is not exclusively due to an increase of the initiation rate, as this would also have resulted in lower molecular weights and in a higher nucleation rate and, thus, in smaller particles (both these effects were not observed; see Figures 12 and 13). In this way, other specific effects obtained combining high-power microwave irradiation and IL that may lead to an increase in the propagation rate and/or decrease of the termination rate cannot be excluded. These effects were not completely elucidated, but may possibly be linked to the greater conductivity of the IL, and ultimately the power dissipation per unit volume of the sample, as discussed before, which may increase the polymerization rates. Further studies including different ILs and conditions should be carried out to validate this hypothesis.

CONCLUSIONS

The results of this study show the advantages of using microwave-assisted processes instead of conventional heating. In addition, the investigation shows for the first time that it is possible to combine ILs and microwave irradiation to obtain polymeric latex. The IL [C_{12}mim]Cl was efficiently used as latex surfactant in substitution to DTAB during emulsion polymerization of MMA. Specific effects linked to IL–microwaves interactions were mainly found for reactions using high-power microwave irradiation, where slightly higher conversions and molecular weights could be obtained. General microwave-assisted polymerization reactions, performed with constant temperature, using ILs yielded similar results to those reactions conducted with a typical surfactant (DTAB). These results are of high importance because they clarify that ILs can maintain their surface activity, providing appropriate stability to the polymeric particles in the latex, even in the presence of electromagnetic field. It should be highlighted that to date, ILs have been essentially used in combination with microwave technology as solvents for solution polymerizations because of their high polarity and dielectric properties, which favor intensive movement of species with the applied magnetic field and intense absorption of microwave energy. It was shown in this study that even in the presence of electromagnetic field, increasing concentrations of IL accelerate the polymerization reactions, resulting in stable polymeric latex.

ACKNOWLEDGMENTS

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