Macromol. Symp. **2011**, 302, 161–168 DOI: 10.1002/masy.201000060

Microwave Effects Due to Anionic or Cationic Initiators in Emulsion Polymerization Reactions

Cristiane Costa,[1] *Verusca H. S. Santos,*[2] *Claudia Sayer,**[1] *Pedro H. H. Araujo,*[1] *Alexandre F. Santos,*[2,3] *Montserrat Fortuny*[2,3]

Summary: Emulsion polymerization reactions were performed under microwave irradiation and conventional heating using anionic or cationic initiators and surfactants. Microwave irradiation promoted higher reaction rates for both initiators and surfactants, in comparison with the conventional heating. The effect of high power microwave irradiation was studied using a method of cycles of heating and cooling, where rapid polymerization reactions were obtained. In the reactions with anionic initiator and surfactant, a decrease in the particle diameters was observed with microwave heating, and even smaller particles were obtained using high power microwave irradiation. Moreover, the decrease in the particle size was acompanied by an increase in the polymer molecular weight. On the other hand, these effects were not observed for reactions with cationic initiator and surfactant.

Keywords: anionic initiators and surfactants; cationic initiators and surfactants; emulsion polymerization; kinetics; microwave irradiation

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. As a result, the heating rate and efficiency of microwave heating strongly depend on the dielectric properties and the relaxation times of the reaction mixture.[1]

In emulsion polymerization reactions, microwave heating has been extensively used, showing the advantages of rapid reactions, higher yields and low energy consumption.[2–8] Most of the studies that have been published aiming at the emulsion polymerization, support the idea that the microwave irradiation increases the initiator decomposition rates and the final conversion of certain monomers.[4–8] In this sense, some initiator decomposition reactions have been also studied using microwave irradiation.[3,5–7,9–11] Zhu et al.[3] obtained higher potassium persulfate (KPS) decomposition rates using the microwave heating (about 3 times higher) when compared with the decomposition rates obtained using the conventional heating method. Similarly, Li et al.[3] obtained KPS decomposition rates 4.8 times higher when using the microwave heating method at 110 °C. Costa et al.[10] performed KPS decomposition reactions at temperatures between 60 and 80 °C, and observed decomposition rates about 3-4 times higher with microwaves, depending on the reaction temperature. In another study using the cationic initiator 2-2′-azobis(2-methylpropionamidine)dihydrochloride (V50) in decomposition reactions conducted at temperatures between 60 and 80 °C, Costa et al.[11] obtained decomposition rates about 3-5 times higher under microwave irradiation, compared with that obtained under conven-

---

[1] Departamento de Engenharia Química e de Alimentos, Universidade Federal de Santa Catarina, Florianópolis SC, 88040-900, Brazil
E-mail: csayer@enq.ufsc.br

[2] Núcleo de Estudos em Sistemas Coloidais, Instituto de Tecnologia e Pesquisa, Aracaju SE, 49032-490, Brazil

[3] Programa de Engenharia de Processos, Universidade Tiradentes, Aracaju SE, 49032-490, Brazil

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

tional heating. With regard to the acceleration of emulsion (and miniemulsion) polymerization reactions under microwave irradiation, increased reaction rates were found for a number of monomers, including styrene,[2,7,12,13] methyl methacrylate[4,5,8,14,15] and butyl methacrylate.[6]

This work compares the effect of microwave irradiation in emulsion polymerization reactions with anionic or cationic initiators and surfactants. Methyl methacrylate polymerizations, using the initiators potassium persulfate or 2-2′-azobis(2-methylpropionamidine) dyhidrochloride were carried out in both conventional water bath heating and microwave heating. The effect of high power microwave irradiation in emulsion polymerizations was also studied. For this purpose, pulsed reactions were conducted, in which the samples were repeatedly heated from room temperature to 80 °C through microwave irradiation at 1400 W, within short intervals of time and cooled down in an ice bath immediately afterwards.

Experimental Part

Materials

The monomer used was methyl methacrylate (MMA), of analytical grade, obtained from Merck. 2-2′-azobis(2-methylpropionamidine)dihydrochloride (V50) and dodecyltrimethylammonium bromide (DTAB) were purchased from Sigma-Aldrich and used as cationic initiator and surfactant, respectively. Potassium persulfate (KPS), from Vetec, was the anionic initiator. Anionic surfactant Disponil FES32 and nonionic surfactant Disponil A3065 were obtained from Cognis and used in anionic reactions. Deionized water was used as continuous medium. All reagents were used directly as received, without further purification.

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, each 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 prior to 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.

Polymerization Reactions

Initially, emulsion polymerization reactions were performed under constant temperature (80 °C). To proceed with the polymerizations, four reactor vials were filled each with 20mL of a previously prepared emulsion based on the formulations shown in Table 1, and purged with nitrogen during 30 minutes. Thereafter, the vials were closed with screw caps and submitted to microwave irradiation during specific reaction times. The vials were promptly heated up to the reaction temperature and, after being kept at 80 °C for a certain time interval, the samples were collected and 3 drops of an aqueous hydroquinone solution (1 wt.%) were added to fully stop the reaction. Sampling during the reactions was not possible because the

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1.
Formulations of the polymerization reactions.

Reaction	Reagents (wt.% related to total mass of the reaction mixture)				
	Initiator	Surfactant (ionic)	Surfactant (nonionic)	Monomer	Deionized water
Anionic	0.017	0.14	0.50	19	80
Cationic	0.013	0.57	–	20	79

vials with the reaction medium were kept closed. In this way, each collected sample corresponds to an independent reaction.

Pulsed microwave reactions were carried out to investigate the effect of high power microwave irradiation in emulsion polymerizations. After purging the 20 mL of the previously prepared emulsion (formulations shown in Table 1) with nitrogen during 30 minutes, the samples were repeatedly heated from room temperature to 80 °C through microwave irradiation at constant power (1400 W), within short intervals of time. Each microwave irradiation pulse was of about 30 seconds, which was just the time needed to heat the reaction medium from room temperature to 80 °C. The samples were cooled down in an ice bath for 4 minutes between microwave irradiation pulses. Experiments were carried out applying 1 to 8 irradiation pulses. After each procedure, samples were collected and 3 drops of an aqueous hydroquinone solution (1 wt.%) were added to fully stop the reaction.

In order to evaluate the microwave effects in the emulsion polymerization reactions, conventional heated reactions were carried out at constant temperature (80 °C) using a 500 mL jacketed glass reactor, equipped with a mechanical stirrer, a nitrogen inlet, a thermocouple (type J) and a condenser. Water, monomer and surfactant were added into the reactor, stirred at 300 rpm and heated up to 80 °C. In order to remove oxygen, the medium was purged with nitrogen at a low flow rate throughout the entire process. The initiator (KPS or V50) dissolved in water was added and the temperature was kept constant. Samples were taken out at regular intervals of time and 3 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 1).

Characterization

Monomer conversions were calculated from the ratio of polymer weight and initial monomer weight. 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 1:15 with distilled water. Morphology of the final polymer particles was analyzed by transmission electron microscopy (TEM – JEOL JEM 2100). Several drops of the diluted samples (1:10) were placed on a 300 mesh Formvar copper grid. After drying samples were sputter-coated with a thin carbon film to avoid the degradation of the PMMA under the electron beam and observed at 100 kV. The free software Size Meter, developed at the Chemical and Food Engineering Department of the Federal University of Santa Catarina, was used for the determination of the particle size distribution. 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 1.0mL/min, at 35 °C), and calibration was done using polystyrene standards ($Mw = 580/9.225 \times 10^6$).

Results and Discussion

In Figure 1 it is observed that microwave-assisted polymerization reactions with

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

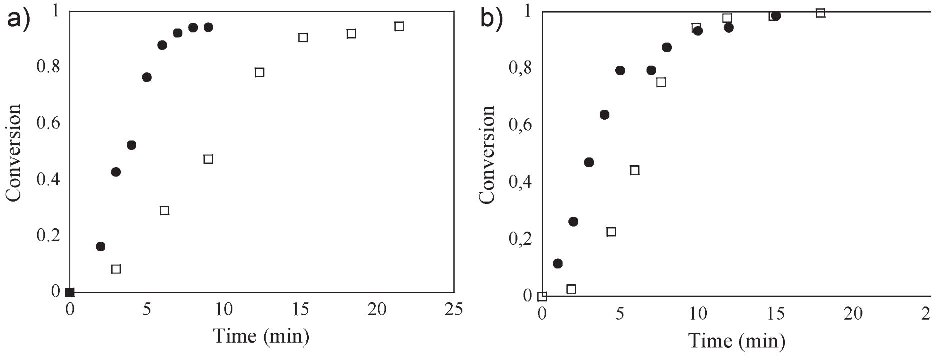

Figure 1.
Evolution of conversion during MMA emulsion polymerizations with microwave (●) and conventional (□) heating at constant temperature 80 °C: (a) anionic; (b) cationic.

constant temperature were faster than the conventional ones, for reactions with both anionic and cationic initiators and surfactants. This acceleration can be ascribed to the increase in the initiator decomposition rates under microwave irradiation. A previous work showed that the decomposition rate constant of the anionic initiator KPS is about 3–4 times higher when using microwaves, compared with the conventional heating.[10] Similarly, the microwave irradiation promotes increase of 3–5 times in the decomposition rate constant of the cationic initiator V50.[11] However, the enhancement in the polymerization reaction rate due to microwave irradiation was more pronounced in the reaction with anionic initiator and surfactant, what can be related to the microwaves effect on the polymer particles size, as shown later in Figure 3a.

Emulsion polymerizations carried out with cycles of heating and cooling, using microwave irradiation with constant power of 1400 W, are shown in Figure 2. It is observed that rapid reactions were obtained with this method of cycles using both anionic and cationic initiators and surfactants. For the performed anionic reaction, 95% of conversion was obtained with only 7 pulses of microwave irradiation (about 30 seconds each pulse). Similarly, in the reaction with cationic initiator and surfactant, 7 pulses of microwave irradiation resulted in 90% of conversion.

Figure 3 presents the evolution of the intensity average particle diameters obtained in polymerization reactions, under micro-

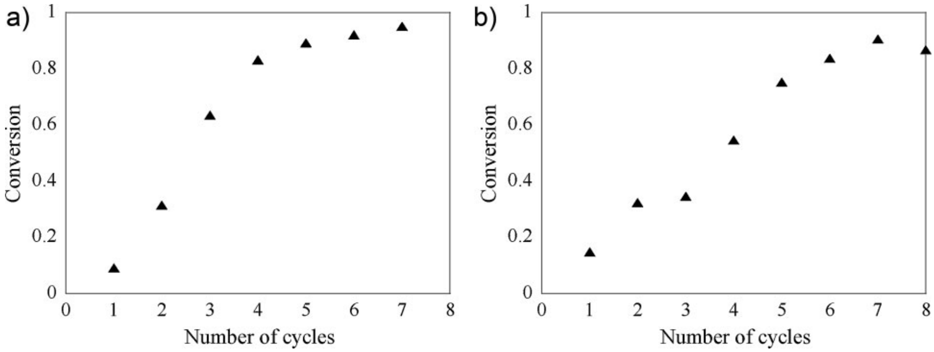

Figure 2.
Evolution of conversion during MMA emulsion polymerizations with cycles of cooling and heating under microwave irradiation: (a) anionic; (b) cationic.

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

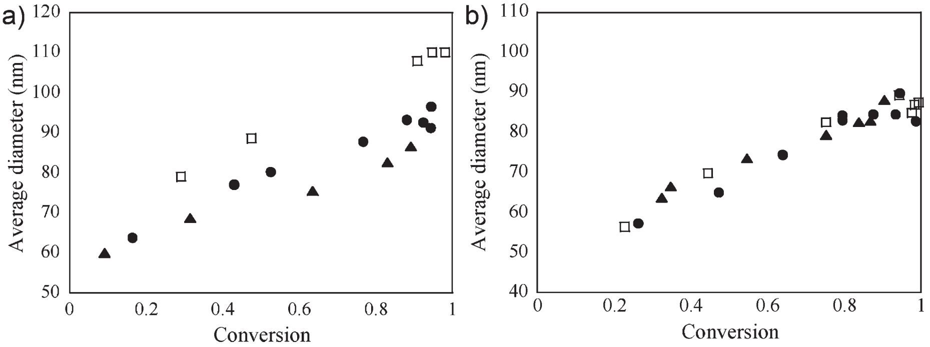

Figure 3.

Evolution of average diameter of polymer particles during MMA emulsion polymerizations with microwave (●) and conventional (□) heating at constant temperature 80 °C, and with cycles of cooling and heating under microwave irradiation (▲): (a) anionic; (b) cationic.

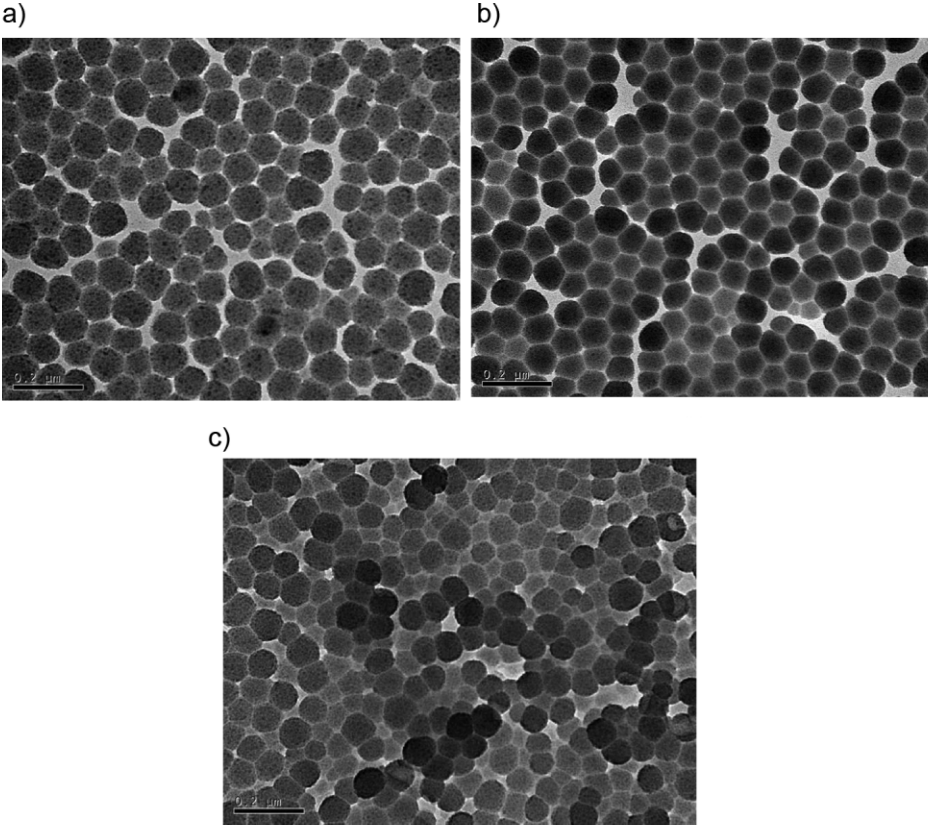

Figure 4.

TEM micrographs of PMMA particles obtained in emulsion polymerizations using anionic initiator and surfactant: (a) conventional heating; (b) microwave heating at constant temperature 80 °C; (c) cycles of cooling and heating under microwave irradiation.

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

wave and conventional heating with constant temperature and under microwave irradiation with constant power. It is observed in Figure 3a that, in reactions with anionic initiator and surfactant, the polymer particles obtained with microwave irradiation were smaller than those obtained with conventional heating. Moreover particles obtained with the method of cycles were the smallest ones. This result can be ascribed to enhancements in KPS decomposition rates, leading to fast nucleation of a higher number of particles, observed with microwaves under constant temperature and also with constant power.[10] The size of the particles formed during reactions with cationic initiator and surfactant was similar for the three heating methods studied. So, in these polymerizations, the increase in V50 decomposition rates under microwave irradiation, reported elsewhere,[11] might be the cause of acceleration in the emulsion polymerizations, as presented above, but in this case did not affect the diameter of the polymer particles.

This difference in the effect on particle diameters between reactions with anionic or cationic initiators and surfactants can possibly be ascribed to the surfactant concentration used in these reactions. For reactions using the anionic initiator, in which a microwave effect was observed on the particle diameters, the concentration of surfactant was much greater (8 times higher) than the CMC value (CMC = 0.10 mM for the mixture of Disponil FES32 and Disponil A3065 used in these reactions). For the reactions with cationic initiator, on the other hand, the concentration of surfactant (DTAB) was only 1.86 times greater than the measured CMC (12.6 mM) for this

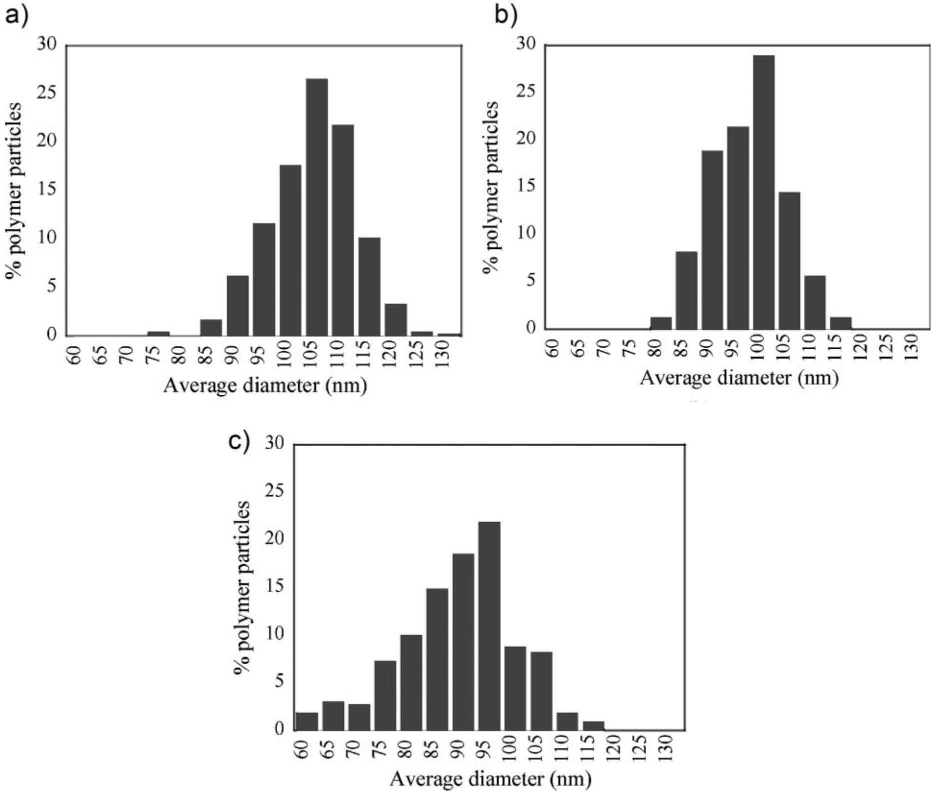

Figure 5.

Particle size distributions of PMMA particles obtained in emulsion polymerizations using anionic initiator and surfactant: (a) conventional heating; (b) microwave heating at constant temperature 80 °C; (c) cycles of cooling and heating under microwave irradiation.

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

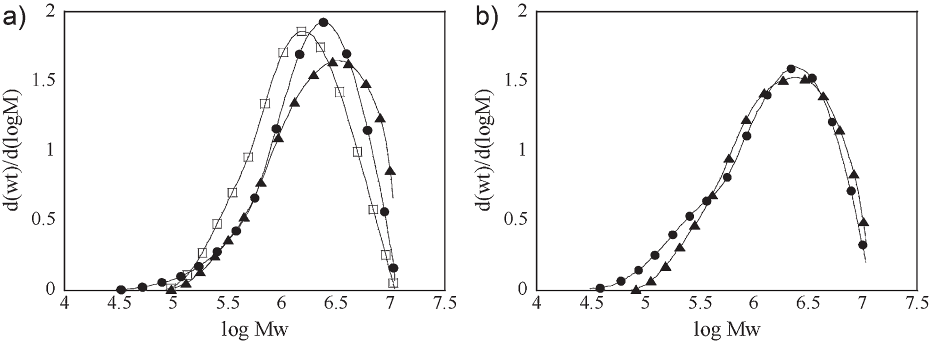

Figure 6.
Molecular weight distributions of the polymers obtained in MMA emulsion polymerizations with microwave (●) and conventional (□) heating at constant temperature 80 °C, and with cycles of cooling and heating under microwave irradiation (▲): (a) anionic; (b) cationic.

surfactant. In this way, the reduced concentration of surfactant may hamper the increase of the number of stable particles in these reactions with microwave enhanced initiator decomposition.

TEM micrographs of the final polymer particles obtained in reactions with anionic initiator and surfactant are shown in Figure 4. Spherical and uniform particles were obtained with the three heating methods studied. However, it is observed in Figure 4c that the polymer particles formed with cycles of cooling and heating under microwave irradiation were more polydisperse than the other ones. This can be due to successive heating and cooling applied in this method, what can extend the nucleation stage, leading to the formation of particles in different reaction times.

The particle size distributions obtained from TEM images are presented in Figure 5. Monodisperse distributions were observed for the three heating methods, with a broader distribution in the reaction with cycles of heating and cooling under microwave irradiation (Figure 5c).

Figure 6 and Table 2, show, respectively, the molecular weight distributions and the number (*Mn*) and weight (*Mw*) average molecular weights of the polymers obtained in reactions with anionic and cationic initiators and surfactants, under microwave and conventional heating with constant temperature and under microwave irradiation with constant power. It is observed that, for reactions with anionic initiator and surfactant (Figure 6a), the molecular weight of polymer obtained under microwave irradiation was slightly higher than the molecular weight of polymer produced with conventional heating. In addition, the molecular weight of polymer obtained with cycles of heating and cooling under microwave irradiation was higher than that obtained with microwaves at constant temperature. The observed enhancement in the molecular weight with microwaves can be a result of the decrease on particle diameters induced by high power microwave irradiation, as shown in Figure 3. Due to radical compartmentalization, the decrease on the polymer particle diameters

Table 2.
Number average molecular weight (*Mn*) and Weight average molecular weight (*Mw*) for polymers obtained in reactions with anionic or cationic initiators and surfactants.

	Anionic		Cationic	
	Mn ($\times 10^3$)	Mw ($\times 10^3$)	Mn ($\times 10^3$)	Mw ($\times 10^3$)
Conventional	854	2172		
Microwave	970	2919	641	2557
Microwave with cycles	1273	3544	950	2958

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

can promote an increase in the polymer molecular weight. This effect was less pronounced in reactions using cationic initiator and surfactant (Figure 6b).

Conclusion

The use of microwave heating promoted faster methyl methacrylate emulsion polymerization reactions compared with the conventional ones. For both anionic and cationic initiators (KPS and V50), reaction rates were higher in reactions using microwave irradiation. These results agree with the enhanced decomposition rate of both initiators reported in previous works.[10,11] In the microwave heated polymerizations with the anionic initiator a decrease was observed in the polymer particles size, compared with the conventional reaction. Moreover, in the reaction with cycles of cooling and heating under microwave irradiation, besides of resulting in even smaller particles, also had a broader particle size distribution. In addition, in these reactions the decrease of particle size was accompanied by an increase in the molecular weight. In microwave heated polymerizations with the cationic initiator and surfactant, on the other hand, no effect was observed on particle size. This can possibly be ascribed to the lower concentration of cationic surfactant used in these reactions. Results show the differences in the two studied systems and the advantages of using microwave irradiation to perform these polymerization reactions.

[1] A. Hoz, Á. Diaz-Ortiz, A. Moreno, *Chem. Soc. Rev.* **2005**, *34*, 164.
[2] R. Correa, G. Gonzalez, V. Dougar, *Polymer* **1998**, *39*, 1471.
[3] J. Li, X. Zhu, J. Zhu, Z. Cheng, *Rad. Phys. Chem.* **2007**, *76*, 23.
[4] J. Sierra, J. Palacios, E. Vivaldo-Lima, *J. Macromol. Sci.* **2006**, *43*, 589.
[5] J. Bao, A. Zhang, *J. Appl. Polym. Sci.* **2004**, *93*, 2815.
[6] W.-D. He, C.-Y. Pan, T. Lu, *J. Appl. Polym. Sci.* **2001**, *80*, 2455.
[7] X. Zhu, J. Chen, Z. Cheng, J. Lu, J. Zhu, *J. Appl. Polym. Sci.* **2003**, *89*, 28.
[8] X. Zhu, J. Chen, N. Zhou, Z. Cheng, J. Lu, *Eur. Polym. J.* **2003**, *39*, 1187.
[9] H. M. Jung, Y. Yoo, Y. S. Kim, J. H. Lee, *Macromol. Symp.* **2007**, *249–250*, 521.
[10] C. Costa, V. H. S. Santos, P. H. H. Araujo, C. Sayer, A. F. Santos, M. Fortuny, *Eur. Polym. J.* **2009**, *45*, 2011.
[11] C. Costa, V. H. S. Santos, P. H. H. Araujo, C. Sayer, A. F. Santos, C. Dariva, M. Fortuny, *J. Appl. Polym. Sci.* **2010**, (in press).
[12] C. Holtze, M. Antonietti, K. Tauer, *Macromolecules* **2006**, *39*, 5720.
[13] C. Holtze, K. Tauer, *Macromol. Rapid Commun.* **2007**, *28*, 428.
[14] R. Hoogenboom, U. S. Schubert, *Macromol. Rapid Commun.* **2007**, *28*, 368.
[15] C. Costa, A. F. Santos, M. Fortuny, P. H. H. Araujo, C. Sayer, *Mat. Sci. Eng. C*, **2009**, *29*, 415.

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim