Continuous Inverse Microemulsion Polymerization

ALBERTO SÁENZ DE BURUAGA,* JOSÉ C. DE LA CAL, JOSÉ M. ASUA

Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo 1072, 20080 San Sebastián, Spain

ABSTRACT: The inverse microemulsion polymerization of 2-methacryloyl oxyethyl trimethyl ammonium chloride (MADQUAT) in a continuous stirred tank reactor is investigated. The effect of removing the oxygen from the feed tank, initiator concentration, aqueous phase volume/emulsifier volume ratio, and residence time on the monomer conversion, particle size, and molecular weight was investigated. The removal of the oxygen allowed high conversions with moderate amounts of initiator to be obtained. In general, the process did not present oscillations. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1341–1348, 1999

Key words: inverse microemulsion polymerization; 2-methacryloyl oxyethyl trimethyl ammonium chloride; redox initiation; nucleation; continuous stirred tank reactor

INTRODUCTION

Microemulsions are thermodynamically stable dispersions produced by using surfactants able to reduce the interfacial energy to values close to zero. Both oil-in-water (direct) and water-in-oil (inverse) microemulsions can be produced, but higher volumes of the disperse phase can be attained using inverse microemulsions.[1] The polymerization of inverse microemulsions of aqueous solutions of water-soluble monomers is an attractive way to produce high-molecular-weight water-soluble polymers that can be used advantageously as flocculants in wastewater treatment and enhanced oil recovery.[2–4] Sáenz de Buruaga et al.[5] studied the kinetics of the inverse microemulsion polymerization of 2-methacryloyl oxyethyl tri-

methyl ammonium chloride (MADQUAT) initiated by ultraviolet (UV) light in the presence of azobisisobutyronitrile (AIBN). It was found that high-molecular-weight water-soluble polymers could be obtained in short process times in a batch reactor. The implementation of the process in tubular reactors under conditions similar to those used in the batch reactor would require the UV irradiation of the whole tube, but this will deteriorate the heat transfer characteristics of the system. The alternative of irradiating only in some points of the reactor was checked, and it was found that polymerization stopped shortly after the cessation of the irradiation.

In an attempt to find processes easier to be implemented, Sáenz de Buruaga[6] studied different redox initiation systems reporting that polymerization of MADQUAT occurred at a quite fast reaction rate in the presence of sodium metabisulfite. The ability of some reducing agents to initiate the polymerization of different monomers has been reported.[7–9] Mukherjee et al.[7] described that the metabisulfite and bisulfite were able to initiate the aqueous phase polymerization of

methyl methacrylate, ethyl methacrylate, and methacrylic acid, as well as the polymerization of styrene, although a long inhibition period was observed in this case. On the other hand, metabisulfite and bisulfite were unable to initiate the polymerization of acrylonitrile, methyl acrylate, and vinyl acetate. Murkherjee et al.[7] proposed the following reaction mechanism (in aqueous solutions at low concentrations, the metabisulfite is present as bisulfite[10]).

$$CH_2{=}C + HSO_3^- \rightarrow CH_3{-}C^* + SO_3^{*-} \quad (1)$$

where the activity of the $CH_3{-}C^*X{-}CH_3$ radical is sterically reduced. Actually, the low reactivity of this radical is what makes possible the initiation of methacrylates by the bisulfite. Other vinylic monomers ($CH_2{=}CHX$) also react with the bisulfite, but the radicals formed ($^*CH_2{-}CH_2X$ or $CH_3{-}^*CHX$) terminate quickly with the SO_3^{*-} radical. Murkherjee et al.[7] justified the low reactivity of the styrene in terms of its low water solubility.

MADQUAT has a methacrylic group that may react with metabisulfite through a reaction scheme similar to that presented in eq. (1), namely, forming an active radical and another less reactive ($CH_3{-}C^*X{-}CH_3$). This possibility is particularly interesting in the inverse microemulsion polymerization of MADQUAT because both the monomer and the metabisulfite are dispersed in small droplets[5] (10–30 nm in diameter), where they would terminate quickly if both of them were reactive.

Sáenz de Buruaga et al.[11] studied the kinetics of the inverse microemulsion polymerization of MADQUAT initiated by sodium metabisulfite. The effect of the initiator concentration, emulsifier concentration, the amount of the aqueous phase, and the amount of the disperse phase on the polymerization rate, monomer conversion, particle diameter, and the number of polymer particles was studied. It was found that the metabisulfite was able to initiate the polymerization at a low temperature (20°C). In the batch reactor, the polymerization stopped well before the complete conversion of the monomer due to complete consumption of the initiator, which disappeared

according to first-order kinetics, but high conversions were reached in short periods of time when the initiator was fed during the process in a semicontinuous way. This precludes the use of a tubular reactor unless multiple feeds of the initiator along the reactor are considered. This might be difficult as the mass transfer of the initiator from the entering droplets of initiator solution to the polymer particles might be slow. Thus, Sáenz de Buruaga et al.[11] reported that for the semicontinuous process carried out in a stirred tank, the transport of metabisulfite from the droplets of the initiator solution to the particles was diffusionally limited, and that the mass transfer was accelerated by the availability of the emulsifier, that is, by the emulsification of the entering solution of initiator. One would expect that the emulsification of the entering initiator solution in the tubular reactor would be poor, and, hence, the mass transfer limitations significant.

An alternative is to use a continuous stirred tank reactor (CSTR). The main drawback of this reactor is that it suffers from an oscillatory behavior due to intermittent nucleations.[12] Oscillations are deleterious for both product quality and control of the process. Aizpurua et al.[13] demonstrated that a change of the nucleation mechanism (nucleation of monomer droplets in miniemulsion polymerization as compared to either homogeneous or heterogeneous nucleation in conventional emulsion polymerization) may eliminate the oscillations. As nucleation in inverse microemulsion polymerization is very different to that in conventional emulsion polymerization, there is some hope that the system would not oscillate.

In this work, the inverse microemulsion polymerization of MADQUAT in a continuous stirred tank reactor is investigated.

EXPERIMENTAL

Technical grade MADQUAT was supplied by Elf Atochem as a 75% wt/wt aqueous solution. The emulsifier system was a blend of sorbitan sesquioleate (Arlacel 83, ICI Surfactants) and sorbitan monooleate with 20 ethylene oxide groups (Tween 80, ICI Surfactants). Sodium metabisulfite (purity 96%, Panreac) and, in some runs, ammonium persulfate (purity 99%, MERCK) were used as initiators. All these materials were used as supplied. Deionized water and commercial cyclohex-

Table I   Composition of the Reactor Feeds in the Polymerizations in Which the Oxygen Was Not Removed from the Feed Tank

	Composition of Microemulsion Feed (% in Weight with Respect to the Total Mass)					Composition of the Initiator Solution Feed (% in Weight with Respect to the Total Mass)	
Run	MADQUAT	Water	Cyclohexane	Emulsifier	$(NH_4)_2S_2O_8$	Water	$Na_2S_2O_5$
1	14	14	59	13	0.062	90	10
2	14	14	59	13	0.031	95	5
3	14	14	59	13	0.0154	97.5	2.5
4	17.5	17.5	52	13	0.0274	95.5	4.5

ane were used after filtration. The aqueous phase was prepared by diluting two parts (in weight) of the 75% aqueous solution of MADQUAT with one part of water, giving a 50% aqueous solution of MADQUAT. The oil phase was prepared by dissolving the emulsifiers in the appropriate amount of cyclohexane. The inverse microemulsion was formed by mixing both phases under mechanical agitation and sonicating the mixture for 12 min at room temperature using a Branson Sonifier 450 (intensity, 7; duty cycle, 80%). A transparent and stable microemulsion was obtained. The conductivity of the microemulsion was close to that of the cyclohexane, showing that the microemulsion had a globular structure; namely, it was formed by micelles swollen with aqueous phase.

Two series of reactions were carried out. Tables I and II present the recipes used in the first series, in which the oxygen contained in the microemulsion feed tank was not removed. In this case, polymerization did not proceeded with sodium metabisulfite, and ammonium persulfate (which forms a redox pair with the metabisulfite) was

also used. An aqueous solution of sodium metabisulfite was fed into the reactor, whereas the ammonium persulfate was included in the microemulsion feed. In the second series, the oxygen of the microemulsion feed tank was removed by carrying out two cycles of vacuum (final pressure 250 mbar) and purging with high purity ($<$2 ppm of oxygen) nitrogen under gentle agitation (12 cm^3 s^{-1} until reach 1100 mbar). Tables III and IV present the recipes used in the series in which oxygen was removed from the feed tank.

Polymerizations were carried out at 20°C in a 0.4-L continuous, unbaffled, jacketed glass reactor equipped with a turbine stirrer (300 rpm stirring speed) and nitrogen inlet. The monomer microemulsion and the initiator solution were fed in separate streams. The reactor worked without headspace. Samples were collected from the exit tube, and the polymerization short stopped with hydroquinone. Monomer conversion was determined by gas chromatography using butyl acrylate as an internal standard. Particle size was determined by dynamic light scattering (DLS) us-

Table II   Characteristics of the Polymerizations in Which the Oxygen Was Not Removed from the Feed Tank

Run	Microemulsion Feed Flow Rate (cm^3 min^{-1})	Initiator Solution Feed Flow Rate (cm^3 min^{-1})	$(NH_4)_2S_2O_8$ Feed Flow Rate (mol min^{-1})	$Na_2S_2O_5$ Feed Flow Rate (mol min^{-1})	$\tau = V/Q_{mic}$ (min)	$x_{after\ 15\ \tau}$	$dp_{after\ 15\ \tau}$ (nm)
1	22.8	0.1	5.3×10^{-5}	5.3×10^{-5}	20.6	0.96	93
2	22.8	0.1	2.67×10^{-5}	2.67×10^{-5}	20.6	0.96	97
3	22.8	0.1	1.3×10^{-5}	1.3×10^{-5}	20.6	0	no reaction
4	22.8	0.1	2.4×10^{-5}	2.4×10^{-5}	20.6	0.94	108

Table III   Composition of the Reactor Feeds in the Polymerizations in Which the Oxygen Was Removed from the Feed Tank

Run	Composition of Microemulsion Feed (% in Weight with Respect to the Total Mass)				Composition of the Initiator Solution Feed (% in Weight with Respect to the Total Mass)	
	MADQUAT	Water	Cyclohexane	Emulsifier	Water	$Na_2S_2O_5$
5	16.89	16.89	53.2	13	99.53	0.47
6	16.89	16.89	53.2	13	99.05	0.95
7	16.89	16.89	53.2	13	98.1	1.9
8	16.89	16.89	53.2	13	99.05	0.95
9	16.89	16.89	53.2	13	99.05	0.95

ing a Malvern 4700 apparatus at an angle of 90° and with an incident wavelength of 514.5 nm. The latex was diluted to 5% in volume with pure cyclohexane.[5] The number of particles was calculated from the values of the particle size and the monomer conversion, assuming that all the polymer was in the polymer particles and that the water and monomer partitioned according the thermodynamic equilibrium. The partition coefficients were $k_M = k_W = 0.7$.[14] The weight-average molecular weight of two samples (one of $M_W = 220,000$ and the other of $M_W = 1,400,000$) was measured by light scattering using a Malvern 4700 apparatus at 25°C with an incident light of 514.5 nm. These molecular weights covered the whole range of molecular weights obtained in this work. The molecular weights of the other samples were estimated by interpolation ($\eta = a\,M_W^b$) using viscosity measurements of $1M$ NaCl aqueous solutions of the polymer (0.25×10^{-2} g cm^{-3}). A rheometer Methrom ELV-8 with a shear rate of 60 s^{-1} was used in these measurements.

RESULTS AND DISCUSSION

After polymerization, the latexes were stable and transparent. However, due to the larger particle size of the particles and the higher refractive index of the poly(MADQUAT) compared with the monomer, the latexes dispersed more light than the initial microemulsions.

Table II and Figures 1 and 2 summarize the results obtained in the reactions carried out without removing the oxygen from the feed tank. Polymerization could not be started effectively with sodium metabisulfite, and, hence, the following redox pair was used: sodium metabisulfite–ammonium persulfate (1/1 molar ratio). Table II shows that no polymerization was observed at low initiator concentration (run 3) and that the monomer conversion increased to a very high value when the initiator concentration was increased two times (run 2) (Fig. 1). Further increases of the initiator concentration did not result in significant increases of the monomer conversion. Figure

Table IV   Characteristics of the Polymerizations in Which the Oxygen Was Removed from the Feed Tank

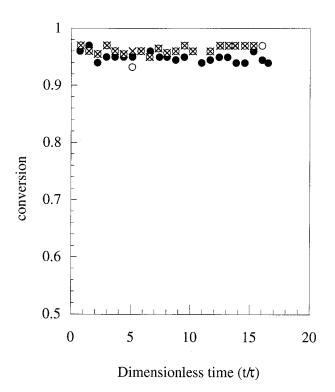| Reaction	Microemulsion Feed Flow Rate (cm^3 min^{-1})	Initiator Solution Feed Flow Rate (cm^3 min^{-1})	Concentration of $Na_2S_2O_5$ in the Feed (mol cm^{-3})	$\tau = V/Q_{mic}$ (min)	$x_{after\ 15\ \tau}$	$dp_{after\ 15\ \tau}$ (nm)
5	26.1	0.115	1.1×10^{-7}	18	0.89	104
6	26.1	0.115	2.2×10^{-7}	18	0.94	107
7	26.1	0.115	4.4×10^{-7}	18	0.96	115
8	32.4	0.14	2.2×10^{-7}	14.5	0.91	107
9	17.3	0.076	2.2×10^{-7}	27.1	0.96	108

Figure 1 Evolution of the monomer conversion in the runs carried out without removing the oxygen from the feed tank: ($\times$) run 1; ($\bigcirc$) run 2; ($\bullet$) run 4.

1 presents the evolution of the monomer conversion. It can be seen that conversion was quite stable in runs 1 and 2 but slightly oscillated in run 4. Figure 2 shows that the initiator concentration had almost no effect on the particle size (dp). On the other hand, the particle size increased as the aqueous phase volume-to-emulsifier volume ratio increased. This agrees with the results obtained in batch[5,14] and semicontinuous processes,[11] although the dependence of dp upon (aqueous phase volume/emulsifier volume) is lower for the CSTR (0.13) than for the batch and semicontinuous reactors (0.66). Figure 2 shows that the particle diameter (and, hence, the number of particles) oscillated during the polymerization carried out with the highest aqueous phase volume-to-emulsifier volume ratio. The reason for this oscillation is not clear, but indications of limited coagulations at high aqueous phase volume-to-emulsifier volume ratios have been found in both batch[5,14] and semicontinuous processes.[11]

The molecular weight in run 2 was 220,000. This is too low for the application of the polymer as a flocculant. The reason for the low molecular weight is that a high concentration of initiator

was used to overcome the inhibiting effect of the oxygen.

Tables III and IV summarize the experiments carried out after removing the oxygen from the feed tank using vacuum and nitrogen purge. In this case, it was possible to work with a lower amount of initiator and using metabisulfite as the only initiator. Hopefully, this would yield higher molecular weights. Figure 3 presents the effect of the initiator concentration on the monomer conversion. It can be seen that high conversions can be achieved using almost 10 times less initiator than in the runs in which the oxygen was not removed from the feed tank (even though, in that case, a mixture of metabisulfite and persulfate was used). Figure 3 also shows that monomer conversion increased with initiator concentration. On the other hand, a limiting conversion ($x = 66\%$) was found when the recipe of run 5 was used in a batch polymerization.[11] The difference is that in the batch process, the initiator disappears early in the process, whereas in the continuous process, there is always initiator in the system as it is continuously fed into the reactor. Figure 4 shows that the particle size decreased with the initiator concentration. This agrees with
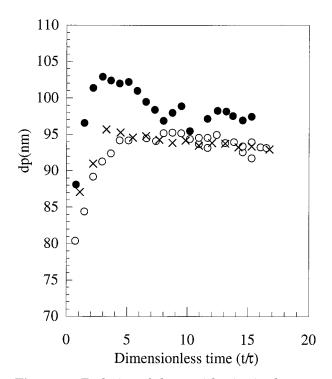

Figure 2 Evolution of the particle size in the runs carried out without removing the oxygen from the feed tank: ($\times$) run 1; ($\bigcirc$) run 2; ($\bullet$) run 4.
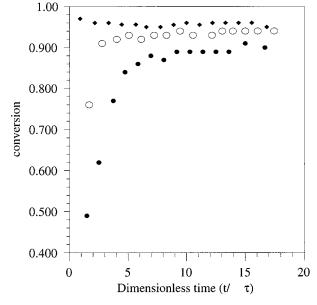
Figure 3 Effect of the initiator concentration on the monomer conversion (experiments carried out after removing the oxygen from the feed tank). Concentration of initiator in the feed: (●) run 5, 1.1×10^{-7}; (○) run 6, 2.2×10^{-7}; (◆) run 7, 4.4×10^{-7}.

what was observed in batch and semicontinuous reactions.[11] The number of polymer particles depended with a power 0.25 upon the initiator concentration.

Table V shows that the molecular weight decreased when the initiator concentration increased. These molecular weights, although substantially higher than the one obtained in the experiment 2, were still low for the application of the polymer as flocculant. On the other hand, the estimated number of polymer chains per particle ranged from 237 in run 5 to 859 in run 7. These values are one order of magnitude higher than those found in the inverse microemulsion polymerization of MADQUAT initiated by UV light in the presence of AIBN[5] and show that each particle captured a large number of radicals (transfer reactions can be ruled out as polymerization stopped shortly after the initiator was consumed[5,11]).

Figure 5 presents the effect of the residence time on the monomer conversion. It can be seen that conversion increased as residence time increased. On the other hand, Figure 6 shows that the residence time had no effect on particle size. In addition, a slight continuous decrease of the particle size was observed during each process.
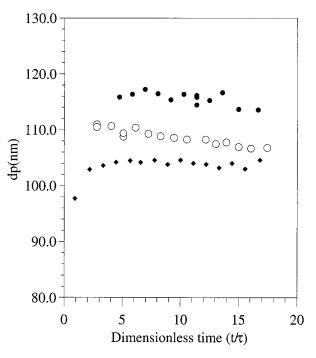

Figure 4 Effect of the initiator concentration on the particle size (experiments carried out after removing the oxygen from the feed tank). Concentration of initiator in the feed: (●) run 5, 1.1×10^{-7}; (○) run 6, 2.2×10^{-7}; (◆) run 7, 4.4×10^{-7}.

CONCLUSIONS

In the foregoing, the inverse microemulsion polymerization of MADQUAT in a continuous stirred tank reactor was investigated. Two series of reactions were carried out. In the first, the oxygen contained in the microemulsion feed tank was not removed. In this case, the polymerization could not be initiated with sodium metabisulfite, and, hence, ammonium persulfate (which forms a redox pair with the metabisulfite) was also used. No

Table V   Viscosities of the Solutions and Estimated Molecular Weights of the Polymers Obtained in the Experiments in Which the Oxygen Was Removed from the Feed Tank

Run	Viscosity (cp)	M_W
5	28	1,500,000
6	21–22	780,000
7	15	310,000
8	19	560,000
9	19–20	560,000–640,000

polymerization was observed at low initiator concentration (run 3), but the monomer conversion increased to a very high value when the initiator concentration was increased twice (run 2). Further increases of the initiator concentration did not result in significant increases of the monomer conversion. Particle size was not affected by the initiator concentration. The runs carried out with low aqueous phase-to-emulsifier ratios did not present oscillations, but cycles were observed when this ratio was increased. Molecular weights too low for the application of the polymer as flocculant were found, likely due to the high concentration of initiator used to overcome the inhibiting effect of the oxygen. In the second, the oxygen of the microemulsion feed tank was removed by using vacuum and nitrogen purge. In this series, high conversions could be achieved using almost 10 times less initiator than in the first series (even though, in that case, a mixture of metabisulfite and persulfate was used). It was found that monomer conversion increased and that molecular weights decreased with initiator concentration. The molecular weights, although substantially higher than in the first series, were still a little bit low for the application of the polymer
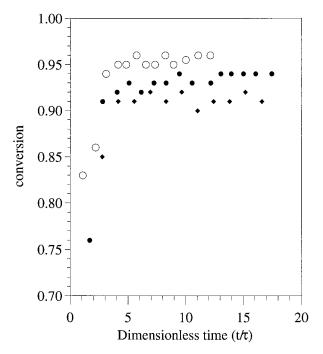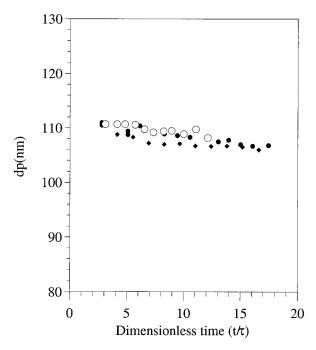

Figure 6   Effect of the residence time on particle size (experiments carried out after removing the oxygen from the feed tank): (●) run 6 (τ = 18 min); (◆) run 8 (τ = 14.5 min); (○) run 9 (τ = 27.1 min).

as flocculant. It was found that conversion increased as residence time increased, but the residence time had no effect on particle size.

Figure 5   Effect of the residence time on monomer conversion (experiments carried out after removing the oxygen from the feed tank): (●) run 6 (τ = 18 min); (◆) run 8 (τ = 14.5 min); (○) run 9 (τ = 27.1 min).

REFERENCES

1. Candau, F. in Polymeric Dispersions: Principles and Applications; Asua, J. M., Ed., Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997.
2. American Cyanamid Co., Eur. Pat. Appl., 0374457, 1990.
3. Institut Français du Petrole, Fr. Pat. Appl., 2565623, 1985.
4. American Cyanamid Co., Eur. Pat. Appl., 0374478, 1990.
5. Sáenz de Buruaga, A.; de la Cal, J. C.; Asua, J. M. J Polym Sci, Part A: Polym Chem 1998, 36, 737.

6. Sáenz de Buruaga, A. Ph.D. Dissertation, Universidad del País Vasco, San Sebastián, Spain, 1998.

7. Mukherjee, R.; Ghosh, P.; Chadhe, S. C.; Palit, S. R. Makromol Chem 1964, 80, 208.

8. Kim, K.; Griffith, J. R. J Colloid Interface Sci 1976, 55, 191.

9. Candau, F.; Leong, Y. S.; Fitch, R. J Polym Sci: Polym Chem Ed 1985, 23, 193.

10. Burns, D. T.; Townshend, A.; Carter, A. H. in Inorganic Reaction Chemistry, Volume 2: Reactions of the Elements and Their Compounds; Ellis Horwood Limited, Chichester, UK, 1981.

11. Sáenz de Buruaga, A.; de la Cal, J. C.; Asua, J. M. Polymer to appear.

12. Kiparissides, C.; MacGregor, J. F.; Hamielec, A. E. Can J Chem Eng 1980, 58, 48.

13. Aizpurua, I.; Amalvy, J. I.; Barandiaran, M. J.; de la Cal, J. C.; Asua, J. M. Macromol Symp 1996, 111, 121.

14. Sáenz de Buruaga, A.; de la Cal, J. C.; Asua, J. M. J Polym Sci, Part A: Polym Chem 1998, to appear.