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Dispersion Copolymerization of Vinyl Monomers in Supercritical Carbon Dioxide

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The thermally initiated free-radical dispersion copolymerization of methyl methacrylate (MMA) and *N,N*-dimethylacrylamide (DMA) in supercritical carbon dioxide has been studied in the presence of polysiloxane surfactants. The formation of a stable latex seems to be related to the presence of at least one reactive end group in the surfactant macromolecule, thus suggesting that anchoring of the stabilizer to the surface of the growing polymer particles occurs through chemical grafting. In the case of a molar ratio of DMA to MMA lower than 0.40, microspherical copolymer particles with yields ranging from 81 to 97% were collected from batch polymerizations carried out at 65 °C and 23−28 MPa using AIBN as an initiator and PDMS-mMA as a surfactant. The effect of conversion on the cumulative composition of the copolymer was investigated at a 0.20 mol/mol DMA/MMA ratio, and this composition, determined through NMR analyses, was found to be roughly constant during the entire process and, at the adopted initial feed composition, to remain close to the initial monomer feed mixture. The effectiveness of the surfactant stabilization toward the growing polymer particles was found to be dependent both on the concentration of the surfactant and on the amount of the hydrophilic monomer (DMA) with respect to the hydrophobic one (MMA). The experimental results indicate that, by a proper selection of the polymerization recipe, it is possible to prepare microspherical copolymer particles with tunable swelling behavior in aqueous media.

Introduction

Supercritical carbon dioxide ($scCO_2$) has been widely investigated in the past decade as a sustainable solvent for chain free-radical polymerization of vinyl monomers.[1,2]

Because only amorphous fluoropolymers, silicones, and polycarbonate−polyether copolymers[3,4] exhibit good solubility in CO_2 under relatively mild conditions ($T <$ 100 °C, $P <$ 35 MPa), heterogeneous polymerization techniques have been used to operate at acceptable values of pressure and temperature. The dispersion polymerization technique is prevalently adopted: the process is initiated homogeneously, and the resulting polymer separates into primary particles whose coagulation is prevented by a surface-active agent (surfactant) that stabilizes the polymer particles as a latex.[5] Through this route, very high molecular weight polymer is synthesized in the form of microspherical particles with a narrow size distribution. Surfactants are amphipatic macromolecules consisting of an anchoring segment that becomes adsorbed on the surface of the polymer particle by grafting and/or physical adsorption and a stabilizing moiety, usually a fluorinated or polysiloxane portion soluble in the continuous phase, whose relative repulsion prevents coalescence.

It is well-known that a pure homopolymer is rarely employed, and most of commercial polymers are indeed copolymers to better match the various requirements imposed by their utilization. Even though most of the research carried out in $scCO_2$ has been focused on the study of homopolymerization reactions, a limited number of copolymerizations have been investigated. Homogeneous processes are mainly devoted to the synthesis of fluorinated and/or organosiloxane polymers soluble in $scCO_2$ by the choice of at least one suitable fluorinated or siloxane comonomer.[6−8]

Among heterogeneous processes, those aimed at the synthesis of high-value polymers such as polycarbonates[9−11] and polyketones[12] from carbon oxides in the presence of suitable transition metal coordination catalysts are the most appealing and most investigated. Heterogeneous chain free-radical copolymerization have been the object of much less interest, and few examples are reported in the literature describing processes performed in the absence of surfactant[13,14] for the in situ preparation of highly cross-linked polymer microspheres and the dispersion copolymerization of selected vinyl monomers to prepare poly(vinyl acetate-*co*-ethylene) latexes[15] and to copolymerize methyl and ethyl methacrylate in the presence of poly(dimethylsiloxane) monomethacrylate macromonomer as a surfactant.[16] In the latter case, the authors found that the obtained copolymers have composition corresponding to the comonomer feed composition under all investigated experimental conditions, and they assumed that this evidence is an indication that the reactivity ratios in $scCO_2$ are similar to those determined in conventional liquid solvents, which are close to 1 for both considered comonomers.

Because a copolymerization process allows one to prepare new macromolecular compounds that can be addressed to specific applications, we have investigated the possibility of adopting a dispersion technique in the presence of polysiloxane surfactants to copolymerize a hydrophobic monomer (methyl methacrylate) with a hydrophilic one (*N,N*-dimethylacrylamide) to obtain microspherical polymer particles whose swelling in aqueous systems can be tuned as a function of the

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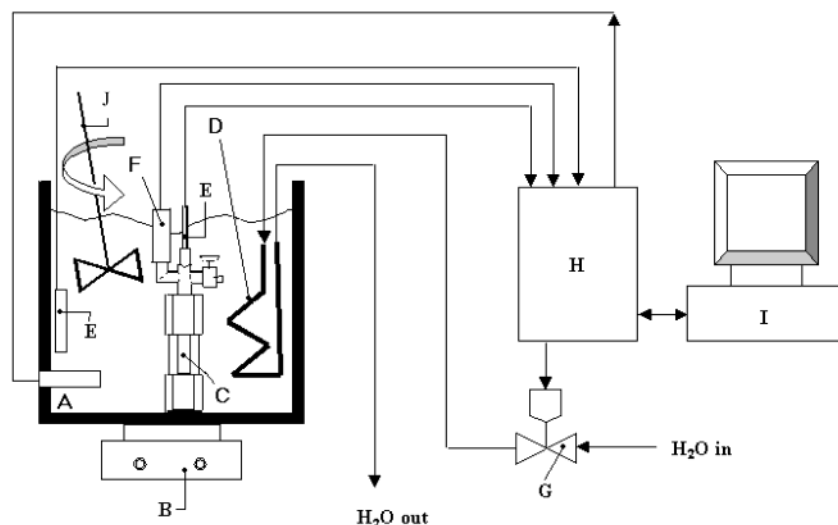
Figure 1. Schematic diagram of the polymerization apparatus: (A) heating electric resistance, (B) magnetic stirrer, (C) reactor, (D) cooling coil, (E) Pt(100) temperature sensor, (F) pressure transducer, (G) electro-valve, (H) control system, (I) computer, (J) mechanical stirrer of the thermostatic bath.

relative amount of the vinyl compound incorporated into the polymer matrix. This approach could be valuable in preparing polymer matrixes for controlled-release systems in aqueous media with suitable release kinetics as a function of the target of utilization.

Experimental Section

Materials. Methyl methacrylate (MMA) and *N,N*-dimethylacrylamide (DMA), obtained from Aldrich, were freshly distilled under vacuum before each test, and 2,2′-azobisisobutyronitrile (AIBN) (Aldrich) and CO_2 (Sol, 99.997 pure) were used as received.

Polysiloxane surfactants were supplied by Aldrich (PDMS-mMA) and TH. Goldschmidt AG (Tegomer surfactants) with the following properties: CH_2=CCH_3—COO—C_3H_6—Si$(CH_3)_2$—[Si$(CH_3)_2$O]$_n$C$_4$H$_9$, PDMS-mMA (M_n = 10 000 g/mol, n = 130); CH_3COO—R—[Si$(CH_3)_2$O]$_n$—Si$(CH_3)_2$—R—OOC—CH=CH_2, Tegomer Sb1783 (M_n = 20 000 g/mol, n = 260); CH_2=CH—COO—R—[Si$(CH_3)_2$O]$_n$—Si$(CH_3)_2$—R—OOC—CH=CH_2, Tegomer Sb1784 (M_n = 20 000 g/mol, n = 260); and CH_3-COO—R—[Si$(CH_3)_2$O]$_n$—Si$(CH_3)_2$—R—OOCCH$_3$, Tegomer Sb1785 (M_n = 20 000 g/mol, n = 260).

Phase Behavior Investigation Apparatus. To study the phase behavior of the CO_2/MMA/DMA mixture under the adopted reaction conditions, a constant-volume view cell was assembled. A stainless steel high-pressure view cell having a volume of 14.5 mL and equipped with two 1-cm-thick sapphire windows with a 180° orientation and 5-cm optical length was used. Temperature control was ensured by inserting the cell into an electronically controlled water bath, while the pressure was recorded by means of a pressure transducer. The cell was subjected to a thermal cycle consisting of a progression of stepwise increases in temperature past the transition value and a similar gradual cooling to room temperature, both achieved with a variation step having an amplitude of 1 °C. After each step, the system was allowed to attain equilibrium before the acquisition of the pressure and temperature values inside the cell. Blank experiments with pure CO_2 demonstrated that equilibrium was reached within 3 min of the thermal perturbation.

Polymerization Apparatus. Experiments were carried out in a stainless steel reactor (total volume of 32 cm³) heated by a water bath controlled by a PID-based cascade control system (Figure 1). The reactor is equipped with a Pt(100) temperature sensor and a pressure transducer whose signals are continuously recorded, together with the temperature of the water in the bath.

After the polymerization, the reactor was quenched in an ice/water bath, and the gas was bubbled in water to trap solid polymer entrained by the fluid. The yield was determined gravimetrically. No purification was necessary before the storage of the polymer product.

Polymer Characterization. Solubility tests were done in a Soxhlet extractor using tetrahydrofuran (THF), close to its boiling point, as the solvent. The extraction time was 24 h.

FTIR analyses were performed on KBr disks containing weighed amounts of the copolymers using a Perkin-Elmer Spectrum 2000 Explorer, taking into consideration the absorbance of the ester carbonyl group —COO— at 1735 cm^{-1} and of the amide carbonyl group —CON— at 1650 cm^{-1}. The measurements were performed by randomly collecting at least two different portions from each polymer sample recovered at the end of polymerization; differences always lower than 5% in the ratios of the absorbances of the aforementioned peaks were observed.

^{1}H NMR analyses were performed in CDCl$_3$ using tetramethylsilane as the internal standard with a Bruker 250 MHz spectrometer to estimate the copolymer composition by the ratio of integration of the methyl ester proton resonances of MMA and the methyl amide substituent proton resonances of DMA.

Molecular weights of the soluble copolymers were determined by GPC using an HP 1100 Chemstation with two PLGel Mixed columns in series, using THF as an eluent against PMMA standards (T = 35 °C, 1 mL/min flow rate, 40-μL injection volume, 0.1% w/v polymer solution), without correction for the different compositions of the macromolecules.

Particle morphologies were analyzed and imaged with a Philips scanning electron microscope (SEM). Samples were sputter-coated with gold to a thickness of ~200 Å. The particle size distributions were evaluated by mea-
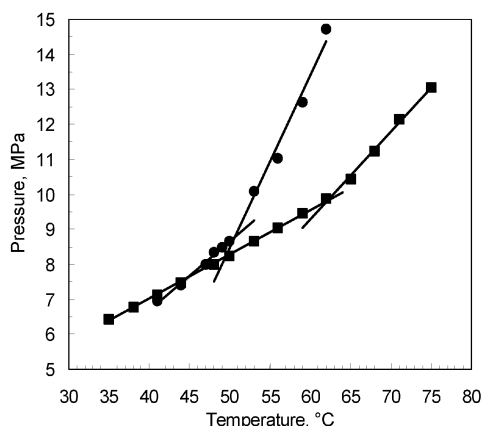
Figure 2. Record of pressure inside the view cell as a function of temperature. A slope variation corresponding to the visual observation of nucleation of a denser phase can be observed. System composition: MMA 13% mol/mol, DMA 3% mol/mol. Density: (■) curve 1, 0.70 g/cm^3; (●) curve 2, 0.75 g/cm^3.

suring at least 100 individual particles from the electron micrographs, and the number-average particle size and particle size distribution were determined.

Results and Discussions

Phase Behavior of the Reaction Mixture. The phase behavior of the CO_2/monomers system was investigated by coupling visual observation of the mixture to the recording of the pressure trend inside the fixed-volume view cell as a function of the temperature during the slow heating and cooling of the system, according to the previously described procedure. At room temperature, all of the investigated systems were composed of two fluid phases, which merged into a single phase during the heating cycle.

The first derivative of P with respect to T at fixed density and composition in the single-phase region is related to the isothermal compressibility κ_{Tx} and isobaric expansion coefficient α_{Px} of the mixture, both computed at constant composition

$$\left(\frac{\partial P}{\partial T}\right)_{v,n_i} = \frac{\alpha_{Px}}{\kappa_{Tx}}$$

At a phase boundary, the compressibility and expansion coefficient of the mixture change. Starting from the one-phase region, the variation of pressure as a function of temperature (Figure 2) is reasonably linear over the limited interval of temperature investigated. When the more dense phase nucleates, the slope of this line changes, and in the two-phase region, the pressure again varies linearly with temperature. An estimation of the transition temperature can be determined by extrapolating both lines until they cross, as shown in Figure 2.

It was observed that, at fixed mole fractions of the components, the higher the average density (defined as the sum of the masses of CO_2, DMA, and MMA divided by the free volume of the view cell) of the reaction system, the lower the value of temperature at which phase nucleation occurs (compare curves 1 and 2 in Figure 2).

This simple static synthetic method was repeated for all initial feed compositions of the reaction mixture adopted in this work, all of which were initially com-

Table 1. Dispersion Copolymerization of MMA and DMA: Effect of the Nature of the Surfactant[a]

entry	surfactant	yield, %	product	D_n,[b] μm	PSD[b]
1	PDMS-mMA	89	powder	3.0	1.09
2	Sb1783	85	powder	4.1	1.02
3	Sb1784	82	powder	3.2	1.01
4	Sb1785	55	hard solid	–	–

[a] MMA 70 mmol, DMA 20% mol/mol based on MMA, stabilizer 5% w/w based on the comonomers, AIBN concentration 0.33% w/w based on the comonomers, CO_2 added in an amount to reach the density of 0.88 g/cm^3; $T = 65$ °C, initial pressure = 26−29 MPa, reaction time = 300 min. [b] D_n = number-average diameter, PSD = D_w/D_n = particle size distribution, D_w = weight-average diameter.

posed of a single phase under the operating conditions adopted to perform the polymerization. The use of the previously described phase behavior investigation to evaluate the initial phase configuration of the reaction system would imply the assumption that the adopted surfactants were used at concentrations low enough to be molecularly soluble in the fluid phase at the T and P values adopted in the polymerization experiments. This assumption could be supported by the results obtained in CO_2/MMA systems for PDMS-mMA[17] and in pure CO_2 for PDMS homopolymers,[18] also taking into account that the effect of the different hydrocarbon terminal portions on the phase behavior of the macromolecules has been found to be negligible.[19] To verify this hypothesis, a set of experiments was repeated in the presence of the surfactant concentration corresponding to the highest amount adopted in the polymerization. We observed that the pressure profile was not substantially altered by the presence of the surfactant. On the other hand, when the DMA/MMA molar ratio was higher than 0.10, the system after the phase transition was initially opaque to visual observation, even in prolonged absence of agitation, and became translucent with increasing temperature. The higher the initial molar amount of the hydrophilic monomer in the system, the higher the value of the temperature at which a clear fluid phase was obtained. This behavior can be attributed to an initial micellization of PDMS surfactants leading to the formation of aggregates having dimensions of the same order of magnitude as the visible light wavelength and consequently to a nonsolvent effect of DMA counterbalancing the well-known solvent effect of MMA toward polysiloxanes. In any case, we observed that, at 65 °C, the surfactant/CO_2/monomers system was always composed of a single transparent phase under all initial mixture compositions used for the copolymerization.

Dispersion Copolymerization. Effect of the Nature of the Surfactant. To test the possibility of adopting PDMS surfactants to perform the copolymerization of MMA and DMA, the process was carried out in the presence of different polysiloxanes using AIBN as an initiator and a DMA/MMA molar ratio of 0.20. The surfactants were selected with different terminal units to obtain indirect information on the mechanism of particle stabilization. All polysiloxane surfactants with at least one vinyl functional terminal unit were found to be effective in the stabilization of the latex dispersion thus leading to the formation of microsphere particles with yields higher than 80% (entries 1−3, Table 1). Polymerization performed in the presence of biacetoxy-terminated PDMS gave lower yields and a hard solid product (entry 4, Table 1), thus indicating

Table 2. Dispersion Copolymerization of MMA and DMA: Effect of the Feed Composition[a]

entry	f^b	$P^{0,e}$ MPa	yield, %	F^b	$M_w,^c$ kg mol^{-1}	$M_w/M_n{}^c$	product	$D_n,{}^d$ μm	PSD^d
1	0.10	27	90	0.102	1130	4.6	powder	3.5	1.04
2	0.20	26	89	0.193	–	–	powder	3.0	1.09
3	0.40	24	81	0.400	–	–	powder	4.7	1.36
4	0	24	93	0	1188	4.1	powder	3.1	1.06
5		26	91		–	–	powder	irregular particles	

[a] Entries 1–4: MMA 70 mmol, PDMS-mMA stabilizer 5% w/w based on the comonomers, AIBN concentration 0.33% w/w based on the comonomers, CO_2 added in an amount to reach the density of 0.88 g/cm³; $T = 65$ °C, reaction time = 300 min. Entry 5: DMA 70 mmol; reaction time = 60 min. All other conditions as in previous entries. [b] f = initial molar ratio of DMA to MMA in the feed, F = molar ratio of DMA to MMA repeat units in the copolymer (^{1}H NMR-determined). [c] M_w = weight-average molecular weight; M_w/M_n = polydispersity index of molecular weight distribution, M_n = number-average molecular weight. [d] D_n = number-average diameter, PSD = D_w/D_n = particle size distribution, D_w = weight-average diameter. [e] P^0 = initial pressure.

that, in the absence of reactive end groups, the polysiloxane macromolecule cannot efficiently adsorb onto the surface of the growing polymer particles. On the basis of these results, it seems reasonable that, for the investigated surface-active compounds and in the case of copolymerization of MMA and DMA, an anchoring mechanism involving chemical grafting through reactive end groups can be postulated.

Dispersion Copolymerization. Effect of the Feed Composition. The study of the effect of feed composition on the dispersion copolymerization of MMA and DMA was performed using PDMS-mMA as a surfactant (entries 1–3, Table 2) and changing the relative amounts of the comonomers at fixed total density of the reaction mixture (0.88 g/cm³) by keeping constant the amount of MMA and increasing the amount of DMA.

Polymer yields higher than 80% were obtained under all adopted experimental conditions. GPC analyses of samples produced in the presence of a low initial mole fraction of DMA showed that the synthesized copolymers had high molecular weights. When the DMA/MMA molar ratio in the feed was higher than 0.10, the polymer was not soluble in THF at 40 °C, thus preventing the possibility of performing chromatographic molecular weight determinations. To ascertain that a copolymer had been obtained, several experimental approaches were adopted.

^{1}H NMR spectra of samples taken from the collected polymer powder were compared with spectra of poly-(MMA) and poly(DMA), both synthesized under similar operating conditions in scCO₂ (entries 4 and 5 in Table 2). A definite shift in the resonance peaks of the methyl ester protons and methyl amide protons can be observed, thus testifying that the two repeat units are incorporated into the same macromolecular chain.

To obtain further evidence of the formation of copolymers, KBr disks prepared by mixing fixed weighed amounts of polymer samples and bromide salt were examined by FTIR spectroscopy. Once again, pure homopolymer samples were used as a reference, and it was possible to observe that the resonance peak of the amide carbonyl group at 1650 cm^{-1} was detected in all samples obtained in the presence of DMA, and its absorbance relative to that of the ester carbonyl group of acrylic derivative repeat unit at 1735 cm^{-1} increased when the initial concentration of nitrogen-bearing vinyl compound increased in the reaction system.

A different portion of the same polymer powders was subjected to solubility tests in boiling THF, which is a nonsolvent for the poly(DMA) homopolymer. All polymers were found to be completely soluble in the solvent. These results, coupled with the FTIR spectroscopic

evidence, furnish a further independent indication that copolymer formation occurred.

In all of the experiments, the polymer was collected in the form of powder composed of particles that gradually deviated from spherical morphology when the mole fraction of DMA was increased. In fact, the presence of a low enough level of the hydrophilic comonomer in the reaction system did not modify significantly the stabilizing effect of the PDMS-mMA macromonomer; on the other hand, when the concentration of N,N-dimethylacrylamide was increased, the PDMS-mMA surfactant seemed less effective in the stabilization of the latex, leading to the formation of polymer particles with higher number-average diameters and wider particle size distributions (Figure 3a–c).

Under all previously described experimental conditions, the composition of the synthesized copolymers was always found to be close to the initial feed composition independently of the yield obtained.

To further investigate this effect, we performed polymerization experiments by stopping different runs at various reaction times, thus limiting the conversion of the comonomer feed. The results, summarized in Table 3, indicate that, whatever the yield values, the copolymer composition, estimated through NMR spectroscopy, remained close to the initial feed composition. This behavior has already been observed in the case of dispersion copolymerization of ethyl and methyl methacrylate[16] and was explained in term of reactivity ratios close to 1 for both comonomers.

In our case, such a circumstance does not seem possible. Indeed, a rough estimation of reactivity ratios for MMA and DMA can be given by using the $Q–e$ scheme,[20,21] which can be considered an empirical approach to placing vinyl monomer reactivity on a quantitative basis. According to this scheme, the reactivity ratios of MMA (comonomer 1) and DMA (comonomer 2) can be given in term of their Q and e parameters, which can be considered measures of the reactivity and polarity, respectively, of a vinyl monomer

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)]$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)]$$

According to the values of Q and e reported in Table 4, values of $r_1 = 1.46$ and $r_2 = 0.44$ were computed, thus
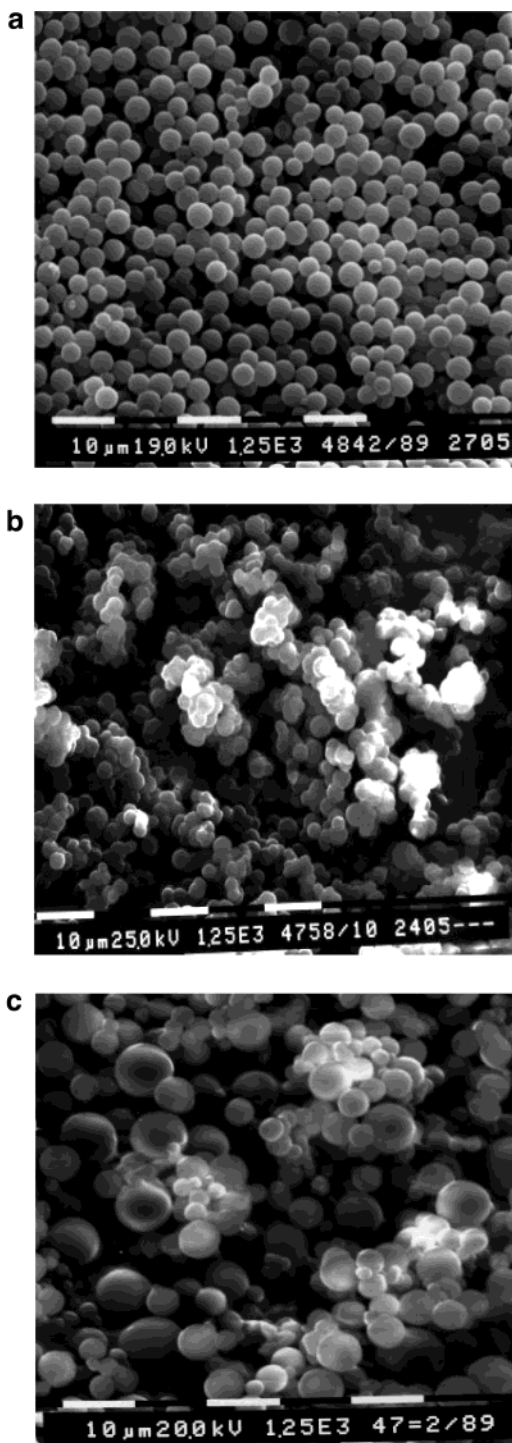
Figure 3. Poly(MMA-*co*-DMA) particles synthesized at different initial molar ratios *f* of DMA to MMA. Experimental conditions as in Table 2. All micrographs are at 1250× magnification. (a) *f* = 0.10, (b) *f* = 0.20, (c) *f* = 0.40.

suggesting that MMA should be incorporated faster than DMA in the copolymer.

On the other hand, we consider relevant the fact that we are dealing with a dispersion copolymerization, so it seems reasonable that the copolymer composition depends not only on kinetic factors but also on the locus of polymerization and on the partitioning of comonomers between the continuous and dispersed phases, so that a constant cumulative copolymer composition can be obtained independently of the values of reactivity ratios. Moreover, this behavior has already been observed in

Table 3. Dispersion Copolymerization of MMA and DMA: Effect of Reaction Time on the Copolymer Composition[a]

f^b	initial pressure, MPa	time, min	yield, %	F^b
0.20	23	45	nd[c]	–
0.20	25	120	12	0.211
0.20	24	180	26	0.184
0.20	23	240	83	0.193

[a] MMA 70 mmol, PDMS-mMA stabilizer 5% w/w based on the comonomers, AIBN concentration 0.33% w/w based on the comonomers, CO_2 added in an amount to reach the density of 0.88 g/cm³; T = 65 °C. [b] f = initial molar ratio of DMA to MMA in the feed, F = molar ratio of DMA to MMA repeat units in the copolymer (^{1}H NMR-determined). [c] nd = not detectable.

Table 4. Q and e Values for Free-Radical Copolymerization of MMA and DMA

monomer	Q^a	e^a
MMA (1)	0.78	0.40
DMA (2)	0.41	−0.26

[a] From Greenley, R. Z. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; Chapter II, pp 267−274.

the dispersion copolymerization of styrene and butyl acrylate in an ethanol−water mixture.[22]

To complete the experimental framework, we investigated the homopolymerization of *N,N*-dimethylacrylamide in scCO₂. We observed that the homopolymer can be synthesized in high yields in a rapid polymerization process (reaction time reduced to about one-quarter of that necessary to achieve similar yields in the copolymerization process) using PDMS-mMA as a surfactant (entry 5, Table 2); SEM micrographs of the collected powders show that it is composed of particles of irregular form and broad size distribution (Figure 4a,b). It is worth mentioning here that two kinds of loss of monodispersity in dispersion polymerization are discussed by Paine:[23] the stabilization of a secondary particle population owing to a faster increasing of grafts available with respect to interfacial surface rate of generation and coalescence of large particles if the number of grafts available is not enough to grant the minimum coverage. A possible explanation of the observed broadening of the particle size distribution (PSD) can be related to the previously described nonsolvent effect of DMA toward PDMS chains, which should favor more coiled conformations, thus leading to an increase in the number of grafts required to stabilize a unit of interfacial surface. According to this picture and considering the high rate of DMA polymerization, the grafting kinetics could be not fast enough to balance the rate of interfacial surface generation, so that particle coalescence occurs to decrease the extent of surface to be stabilized.

Effect of the Surfactant Concentration. A further set of experiments was performed to test the possibility of controlling the particle size of the copolymer latex by modifying the concentration of the polysiloxane macromonomer stabilizer.

Polymerization reactions were performed at two different initial molar ratios of DMA to MMA. In the case of 10% mol/mol DMA/MMA, stabilized microparticles were detected at all investigated concentrations of PDMS-mMA, whose addition to the reaction system leads to a marked decrease in the size of the polymer particles (Table 5). In the case of the dispersion polym-
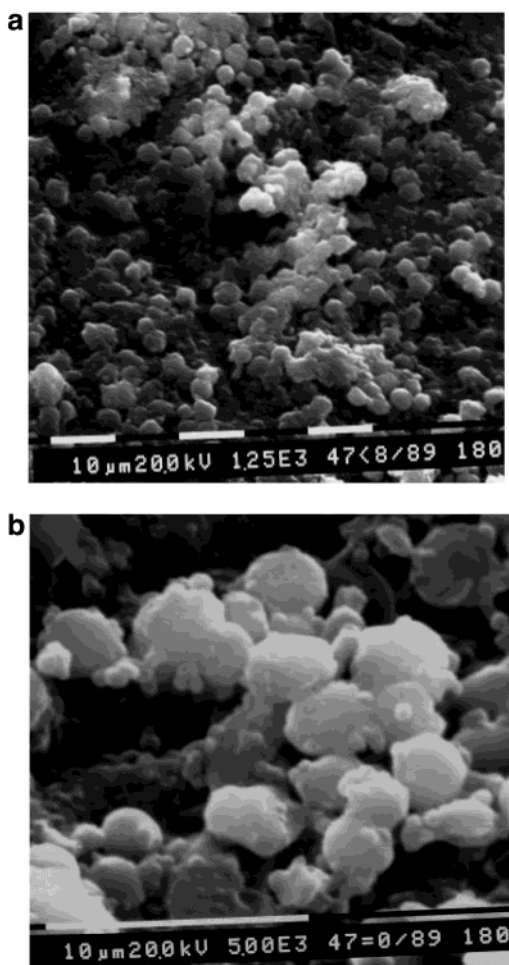
Figure 4. Poly(DMA) particles synthesized in the presence of PDMS-mMA as a surfactant. Experimental conditions as in Table 2, entry 5. (a) 1250× magnification, (b) 5000× magnification.

Table 5. Dispersion Copolymerization of MMA and DMA: Effect of the PDMS-mMA Concentration[a]

f^b	initial pressure, MPa	PDMS-mMA, % w/w[c]	yield, %	D_n,[d] μm	PSD[d]
0.10	28	2.5	89	3.9	1.10
0.10	27	5.0	90	3.5	1.04
0.10	28	7.5	97	1.8	1.02
0.10	27	10.0	95	1.4	1.12
0.10	28	12.5	97	1.2	1.08
0.20	25	2.5	82	highly coagulated	
0.20	23	5.0	83	3.0	1.09
0.20	25	10.0	86	3.6	1.03

[a] MMA 70 mmol, AIBN concentration 0.33% w/w based on the comonomers, CO_2 added in an amount to reach the density of 0.88 g/cm³; $T = 65$ °C, reaction time = 240 min. [b] $f =$ initial molar ratio of DMA to MMA in the feed. [c] Based on the comonomers. [d] $D_n =$ number-average diameter, PSD $= D_w/D_n =$ particle size distribution, $D_w =$ weight-average diameter.
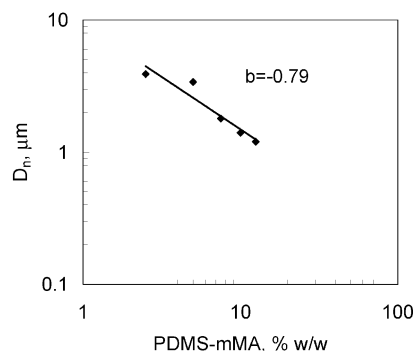

Figure 5. Particle size versus weight fraction of PDMS-mMA macromonomer for copolymerization of MMA and DMA. Experimental conditions as in Table 5 with $f = 0.10$. The points are experimental data; the line is a linear least-squares fit of the points in the log–log plot. Slope $b = -0.79$.

erization of MMA in scCO₂, it was found that the variation of the final diameter as a function of surfactant concentration can be fitted by a power law of the form

$$d = k[S]^b$$

where the value of b obtained from the fitting of experimental data is −0.73, an exponent somewhat larger than the value of −0.50 predicted by the Paine model.[17]

A similar fitting of the number-average diameters of copolymer particles synthesized at 10% mol DMA/MMA is reported in Figure 5, giving an exponent of −0.79, which is rather close to that reported for MMA homopolymerization, so that the addition of such a limited amount of DMA to the reaction system does not seem to perturb the mechanism of the stabilization.

When the initial molar amount of the hydrophilic monomer was further increased, a different effect of the surfactant concentration on particle size was observed. Highly coagulated particles with irregular form were obtained in the presence of 2.5% w/w PDMS-mMA, even though a residual of a spherical morphology could be recognized in the micrographs (Figure 6a). By increasing the surfactant concentration to 5% w/w, a well-defined microspherical powder was collected from the reactor at the end of the polymerization process (Figure 6b), and after an additional increase of the polysiloxane amount,

we once again observed the occurrence of flocculation at some stage during the process, as evidenced by the microsphere coalescence observed in the SEM analyses (Figure 6c). This makes estimation of the particle size somewhat uncertain, which should lead to an underestimation of the true diameters as a consequence of interpenetration of particle edges that are used as reference lines for the visual determination of diameters. Nevertheless, we estimated number-average diameters higher than those obtained in the presence of 5% w/w PDMS-mMA.

During the phase behavior investigation of the reaction mixture, we verified that DMA behaves as a nonsolvent for polysiloxane surfactants, with the consequence that the results obtained at 20% DMA/MMA could probably be due to a more coiled PDMS tail conformation, which shields the acrylic functional unit, thus leading to a decrease in the rate of graft generation.

Evaluation of End-Use Properties of Synthesized Copolymers. As the technical aim of the investigated polymerization process is the preparation of materials with tunable hydrophilicity, the end-use properties of the copolymers obtained at different initial molar ratio of the monomers were compared by measuring their swelling in water. This was done by measuring the weight variation of samples put into contact with water for a fixed amount of time (24 h), assuming that the relative increase in sample volume is proportional to the mass of absorbed water.[24]
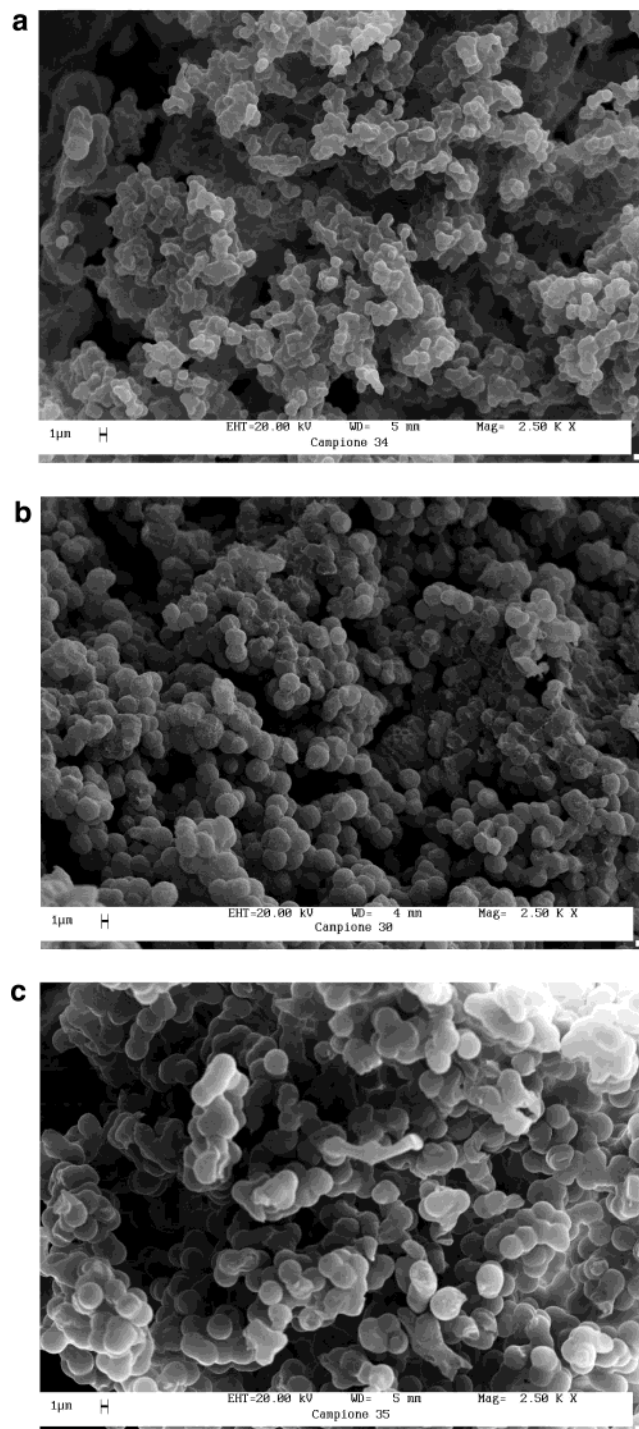
Figure 7. Swelling of copolymer samples obtained at different initial molar ratios f of DMA to MMA exposed to water at 25 °C for 24 h.

Figure 6. Poly(MMA-*co*-DMA) particles synthesized in the presence of different concentrations of PDMS-mMA as a surfactant at $f = 0.20$. Experimental conditions as in Table 5. PDMS-mMA concentrations: (a) 2.5% w/w, (b) 5.0% w/w, (c) 10.0% w/w.

As shown in Figure 7, the copolymers synthesized at higher molar ratios of DMA to MMA are more swollen by water in such a way that it is possible to act on the initial composition of the reaction mixture to control the final property of the material. This result is of relevant interest in the perspective of using such polymeric micropowders as matrixes for the preparation of controlled-release devices. In this case, the release kinetics could be controlled by a proper tuning of the copolymer composition, which is moreover synthesized in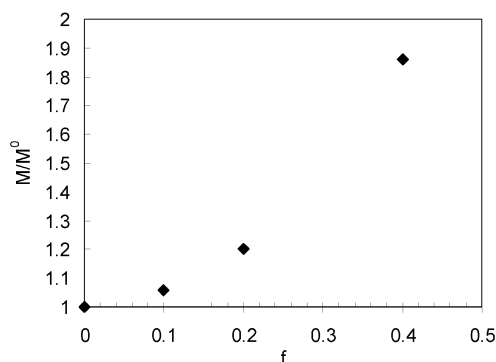 a biocompatible dispersing medium. Additionally, the use of the supercritical fluid makes possible the easy removal of unreacted comonomers simply by modifying the density of the continuous phase to extract from the particles the aforementioned components.

Conclusion

Free-radical copolymerization of methyl methacrylate and N,N-dimehylacrylamide initiated by the thermal decomposition of AIBN can be carried out through a dispersion technique in scCO$_2$, using polysiloxane surfactants with vinyl reactive terminal units as stabilizers, even though phase behavior investigations suggest that DMA behaves as a nonsolvent for polysiloxane chains. High yields of high-molecular-weight copolymers, whose NMR-estimated average composition is always close to the initial comonomer feed composition, were obtained for all investigated feed compositions. This result was also observed in polymerization runs at 20 mol % DMA/MMA stopped at intermediate values of comonomer conversion, reasonably as a consequence of the combined effect of polymerization kinetics and partitioning of comonomers between the continuous and dispersed phases. In the presence of a low enough level of the hydrophilic monomer, the particle size can be controlled by the surfactant concentration; this parameter becomes less effective for this purpose, however, when the DMA loading in the reaction system is increased.

Swelling experiments performed with copolymer samples produced with different initial feed compositions showed that the hydrophilicity of the resulting copolymers can be controlled by the molar ratio of the monomers. This parameter is also relevant in determining the final particle size distribution of the polymer particles, as broader distributions were obtained at increased initial concentrations of the nitrogen-bearing comonomer.

The experimental framework suggests that, through this route, it is possible to obtain solvent-free micronized particles undergoing tunable plasticization in aqueous media that could be used as matrixes for the preparation of controlled-release systems with release kinetics targeted to the end-use application of the composite material.

Acknowledgment

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