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Continuous Reaction System To Investigate the Dispersion Polymerization of Vinyl Monomers in Supercritical Carbon Dioxide

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ABSTRACT: A laboratory-scale continuous reaction system using a stirred tank reactor was assembled in our laboratory to study the dispersion polymerization of vinyl monomers in supercritical carbon dioxide (scCO₂). The apparatus was equipped with a suitable downstream separation section to collect solid particles entrained in the effluent stream from the reactor, whose monomer concentration could be measured online with a gas chromatograph. The dispersion polymerization of methyl methacrylate in scCO₂ was selected as a model process to be investigated in the apparatus. The experiments were performed at 65 °C and 25 MPa with 2,2'-azobisisobutyronitrile as the initiator and a reactive polysiloxane macromonomer as a surfactant to investigate the effect of the mean residence time of the reaction mixture on the monomer conversion, polymerization rate, polymer molecular weight, and particle size distribution. The results were compared with those obtained in batch polymerizations carried out under similar operative conditions. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 4122–4135, 2006

Keywords: dispersions; kinetics (polym.); macromonomers; polysiloxanes; radical polymerization; supercritical carbon dioxide

INTRODUCTION

Because of its favorable chemicophysical and technical–economical properties, supercritical carbon dioxide (scCO₂) has been proposed as an alternative solvent to replace environmentally unfriendly and often more expensive organic solvents for several applications.

Actually, scCO₂, as a green solvent easily separable from less volatile compounds, has already been used on the industrial scale for some extraction processes such as the removal of caffeine from cof-

fee beans, whereas ongoing research is focusing on other interesting applications in the field of particle-forming processes, chromatography, homogeneous and heterogeneous catalysis, and polymer modification processes such as impregnation, dyeing, functionalization, coating, extrusion, and blending.

When we deal with polymerization processes, some important features of scCO₂ are of major relevance. Because of solubility considerations, scCO₂ can be used as a solvent for free-radical homogeneous polymerization only in the case of highly fluorinated amorphous polymers^{1–4} or in the case of organosiloxane polymers,^{5,6} whereas heterogeneous techniques must be adopted in the case of other vinyl monomers. Thus, free-radical heterogeneous polymerizations of many vinyl monomers in scCO₂ have been so far successfully carried out by both

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precipitation^{7–14} and dispersion techniques.^{15–34} In some cases, promising results for forthcoming utilization on the industrial scale were obtained, especially in the case of high-added-value fluoropolymers.

Such potential of scCO_2 as a polymerization medium has been so far mainly evaluated with laboratory-scale batch reactors. Nevertheless, continuous processes can lead to many benefits over batch processes, especially on the industrial scale. From an applicative point of view, they require smaller volumes for equivalent polymer production rates and, hence, lower capital costs, particularly in the case of high-pressure processes. Moreover, the use of smaller reactors increases the safety profile of the process because of the lower holdup of compressed gas as well as the higher heat-transfer rate arising from the higher surface-to-volume ratio of the reactor that can be achieved.

Additionally, continuous polymer removal from the reactor allows a fast reduction of the polymerization kinetics and makes possible the quantitative recovery of the monomer, surfactant, and unreacted initiator with CO_2 as a solvent and swelling agent to perform the extraction from the polymer matrix, thus producing a high-purity product. By this approach, the dispersing agent itself can become the solvent to recycle back to the reactor the surfactant, thus decreasing the impact on the economic evaluation of the process of the high cost of actually available fluorinated or silicone CO_2 -philic stabilizers.

The direct development of processes in a continuously stirred tank reactor (CSTR) with the information obtained in batch experiments can be difficult, mainly because of the problem of evaluating the influence of the residence time distribution on the final product properties. As a result, process development in small laboratory-scale reaction systems based on CSTRs is necessary.

From a scientific point of view, a CSTR-based reaction system is a powerful tool for investigating the kinetics of the polymerization and the mechanism of polymer particle nucleation, thus providing precious information for mathematical modeling of the system that is mandatory to scale up the process from the laboratory to the industrial plant. This consideration is strengthened if we consider that, in the actual state of the art, the main industrial concern toward polymerizations in CO_2 is the manufacture of fluoropolymers, most of which are copolymers. In this context, the use of continuous processes based on well-mixed reactors can become essential to obtaining a copolymer of a fixed composition. Indeed, copolymers synthesized in heteroge-

neous processes in batch or continuous tubular reactors can have very broad composition distributions as a function of the relative reactivities and of the partitioning equilibria of the comonomers. Continuously stirred reactors can allow one to overcome this drawback, provided that they are operated under suitable steady-state conditions.

Continuous polymerization processes in conventional solvents are often performed in stirred tank reactors arranged in a cascade configuration. On the other hand, to the best of our knowledge, the only examples of continuous polymerizations in scCO_2 were reported by DeSimone and coworkers for the precipitation polymerization of vinylidene fluoride^{35–37} and, more recently, of acrylic acid.³⁸ Changing the polymerization technique from precipitation to dispersion by the addition of suitable surfactants can allow easier control of the polymer morphology and molecular weight associated with faster polymerization kinetics. As a result, with dispersion polymerization, high-molecular-weight polymers can be synthesized in scCO_2 in the form of microspherical particles with narrow size distributions.

The effect of the surfactant in a continuous process can be, moreover, essential in ensuring long-term operability of the plant; in fact, it must be considered that a frequent reason for reactor shutdown is the blockage of piping caused by the accumulation of polymer particles in valves and tubing. The surfactant can increase the flowability of the polymer powder, which can be efficiently entrained by the dispersing agent, thus strongly decreasing the probability of obstructions.

In this work, we describe a laboratory-scale reaction system equipped with a CSTR and assembled to study free-radical dispersion polymerizations of vinyl monomers in scCO_2 (Fig. 1). Online analysis of the monomer composition of the effluent stream provided us with information on the monomer conversion and polymerization rate. High-pressure filters were used to recover polymer particles and purify them by extraction with dense CO_2 .

The apparatus was used to study the effect of the mean residence time on the performances of the dispersion polymerization of methyl methacrylate (MMA) in the presence of a siloxane-based macromonomer surfactant.

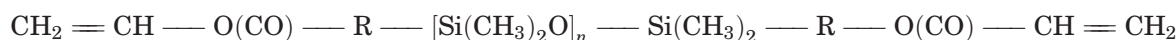
EXPERIMENTAL

Materials

CO_2 (Sol; 99.998% pure), Lab-Scan tetrahydrofuran (THF), Riedel-de Haën cyclohexane, and

benzoquinone from Fluka (purum, $\geq 98.0\%$) were used as received. The liquid solvents were high-performance-liquid-chromatography-grade. The initiator 2,2'-azobis(isobutyronitrile) (AIBN) was purchased from Fluka ($>98\%$), used as received, and stored at $-22\text{ }^{\circ}\text{C}$ to prevent decomposition.

MMA (Aldrich, $>99\%$) was distilled *in vacuo* to remove the inhibitor before each polymerization run.



where R is an alkyl group, n is 260, and the number-average molecular weight is 20,000 g/mol.

Polymerization Apparatus

A schematic representation of the polymerization apparatus is shown in Figure 2. It basically consists of a laboratory-scale CSTR (1) fed with CO_2 , monomer, and polymerization additives (i.e., surfactant and initiator) pressurized at the desired level; the outlet stream flows through the downstream separation units to recover the synthesized polymer, nonreacted monomer, additives, and CO_2 . All lines consist of 1/8- and 1/16-in.-o.d. AISI 316 stainless steel tubes.

A detailed description of each element of the experimental apparatus is given in the following. All numbers in parentheses refer to Figure 2.

Polymerization Reactor

The reactor (Fig. 3), having an internal volume of about 100 mL, is made of AISI 316 stainless

steel and designed to operate up to $200\text{ }^{\circ}\text{C}$ and 45 MPa. Intense internal mixing is achieved by a magnetic coupling (Ken Kimble Mini 100) driven by an electric agitator (Ika RW16 Basic). Two axial two-blade impellers were assembled at different heights on the agitator hub to promote mixing of the supercritical fluid with the dispersed polymer particles in the whole internal volume of the reactor.

As shown in Figure 3, the inlet mixture, composed of CO_2 , monomer, and additives, flows in the thin annular gap of the magnetic coupling, whereas the effluent stream is taken at about mid-height of the reaction chamber, far enough from the inlet door to avoid bypass effects.

The reactor is equipped with a rupture disk, as well as Pt100 temperature sensors to measure both the internal temperature (T_R) and the temperature of the water flowing in the jacket (T_w); a Barksdale UPA3 membrane pressure sensor allows measurements of the internal pressure (p_R).

Reactor control is achieved with an automatic control system that manipulates T_w to keep T_R constant at the set-point value. As shown in Figure 2, the thermostatic water is recirculated in a closed loop (9) connecting the reactor jacket to a suitable bath, whose temperature is controlled with solid-state relays that activate an electric resistance or an electrovalve that allows the flow of cold water in a coil immersed in the bath. All hardware elements (power relays and temperature and pressure sensors) are connected to a personal computer by an Adam 4000 Advantech network interface (8). This device allows us to maintain the reactor temperature at the set-point value within $\pm 0.1\text{ }^{\circ}\text{C}$.

Reactor Feeding System

Liquid CO_2 is compressed with a Maximator model MSF 111DS air-driven pump (2) to the desired pressure, which is finely regulated by means of a Tes-

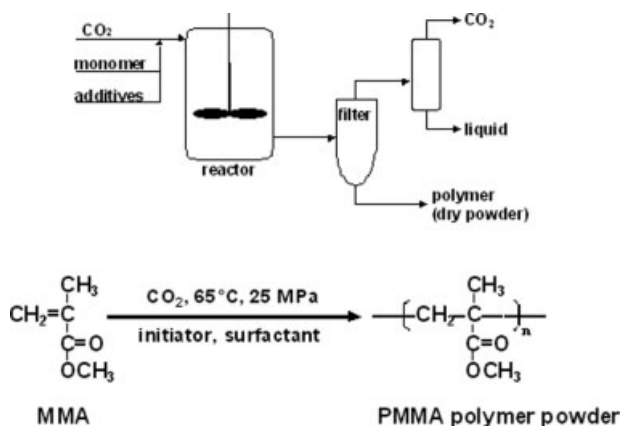


Figure 1. Continuous polymerization of MMA (general process scheme) with AIBN as the initiator and PDMS with a double methacrylic chain end (number-average molecular weight = 20,000 g/mol, $n = 260$) as the surfactant.

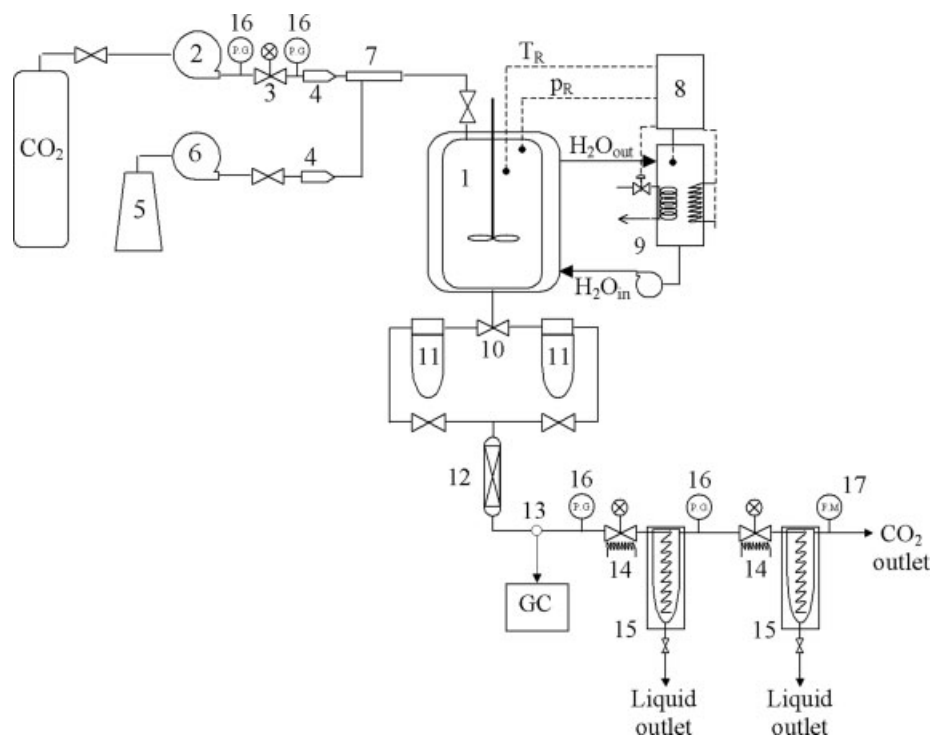


Figure 2. Schematic diagram of the apparatus for continuous heterogeneous polymerization in scCO₂: (1) polymerization reactor, (2) CO₂ pump, (3) pressure reducer, (4) check valve, (5) liquid reactant mixture, (6) liquid pump, (7) static mixer, (8) interface for reactor temperature control, (9) water circulation system for reactor temperature control, (10) three-way ball valve, (11) filter units, (12) packed column (inhibitor), (13) Rheodyne valve for fluid sampling and GC analysis, (14) heated pressure reducers, (15) liquid–gas separation scrubbers, (16) pressure gauges, (17) gas flow meter.

com model 2610 pressure decreaser (3). The pump head is jacketed and cooled with an ethylene glycol aqueous solution to less than 5 °C to avoid cavitation. Before each run, the distilled monomer, surfactant, and initiator are mixed together to obtain a homogeneous liquid phase, which is stored in a vessel under dark at 0 °C under a CO₂ atmosphere (5). This solution is pumped at the desired flow rate with a Gilson model 307 liquid chromatography pump with an SC10 head type (maximum flow rate = 10 mL/min) (6), whose head is jacketed and continuously cooled with cold water. Swagelok check valves (4) with 1-bar reseal pressure are used in this section to prevent backflow. Both liquid streams (CO₂ and monomer mixture) are mixed in a high-pressure static mixer (7) and fed to the reactor at room temperature and the process pressure.

Polymer Separation Units

Because a heterogeneous polymerization takes place in the reactor, the outlet stream from the reactor consists of polymer particles entrained by a CO₂-rich con-

tinuous phase. This heterogeneous mixture is cooled to room temperature in the outlet tube and, through a three-way ball valve (Swagelok) (10), is sent to one of two Headline filter units (11) to trap the polymer particles. The filter housings are made of AISI 316 and designed to operate up to 500 °C and 34 MPa. The filter elements, made of inert silica, allow the quantitative collection (>99.99%) of particles with diameters larger than 0.1 μm. To quench the reaction, both filter housings are jacketed and maintained at temperatures lower than 20 °C by cold-water circulation.

High-efficiency filters are essential not only to recover the synthesized polymer but also to prevent powder deposition in the depressurization section, especially in the pressure-decreasing valves and in the 1/8-in.-o.d. tubes, in which obstructions can occur.

Reaction Quenching and Online Gas Chromatography (GC) Analysis

According to the type I phase behavior exhibited by the CO₂/MMA system,⁴⁰ the compressed fluid

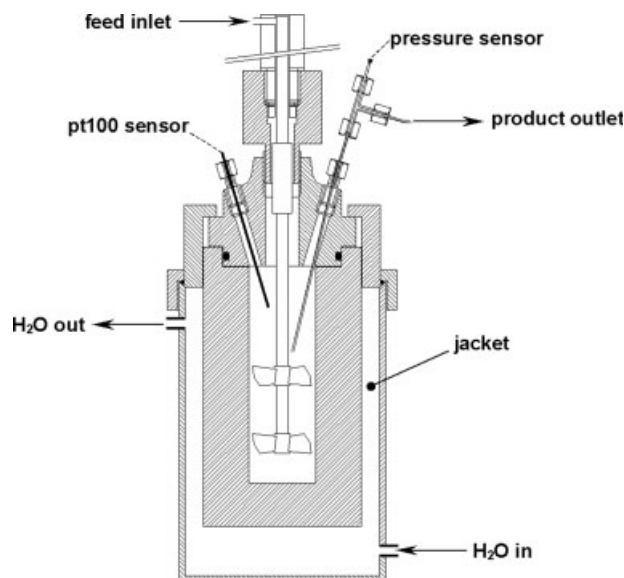


Figure 3. Schematic representation of the polymerization reactor.

leaving the filter units at about 20 °C consists of liquid CO₂ with dissolved nonreacted monomer, surfactant, and initiator. It is passed through a column (12) packed with a free-radical polymerization inhibitor (benzoquinone), so that, after thermal quenching is achieved in the cooled filter units, a chemical quenching of polymerization also is attained to prevent blockages due to polymer formation in the downstream lines and valves. As we have observed that the inhibitor is slightly soluble in liquid CO₂/MMA mixtures, the packed column is periodically reprepared.

Online sampling of the liquid solution from the filters is made with a Rheodyne two-way switching valve (13) with a sampling loop (ca. 1-μL internal volume). The sample consists of liquid CO₂ with dissolved nonreacted monomer and minor amounts of the other components (surfactant, initiator, and CO₂-soluble telomers), and it is sent to a specifically modified PerkinElmer Autosystem gas chromatograph (GC) equipped with a Supelco Carboxpack C column and a Flame Ionization Detector. The sampled fluid is entrained by a nitrogen flow at 0.5 MPa, which is the carrier gas of GC. When the components to be analyzed are not gaseous under room conditions (as in the case of MMA), the injection tube is heated at 130 °C by means of a heating tape. Additionally, to ensure quantitative transfer of the sampled fluid to the GC injector, the sampling valve (13) is maintained for about 4 min in the inject position and afterwards is switched and maintained for about 8 min in the load position (the chromatogra-

phy running time is 12 min). With this procedure, good repeatability has been achieved, with a measured maximum standard deviation in the values of peak areas lower than 4%.

Final Separation and Pressure-Reducing Units

A first pressure reduction is generated by a Tescom pressure decreaser (14) thermostated with a heating tape. The condensed components (i.e., liquids under room conditions) can be continuously collected in a gas-liquid separation drain (15), so that nonreacted monomer along with surfactant and initiator accumulates at the bottom of the scrubber and can be drained with needle valves. A second Air Liquide pressure reducer is used to bring CO₂ under atmospheric conditions and to regulate its flow rate, which is measured under room conditions with a Bronkhorst model F-11C-GD-00-V electronic flowmeter equipped with a Seneca model S164 totalizer (17). For the complete removal of the traces of nonvolatile components from CO₂, a second glycol-cooled separator (<−10 °C) is added in the low-pressure line (Fig. 2).

Procedures

MMA was distilled *in vacuo* and passed through an activated alumina column to remove the inhibitor and water. The presence of inhibitors in the monomer used in a continuous process can significantly hinder the polymerization and even lead to the suppression of the reaction; this is completely different from what happens in a batch process, in which only an induction period can be observed.

Before each polymerization run, leak tests of the reactor were always made. Then, a mixture of CO₂, MMA, Sb1784, and AIBN, at the same composition and flow rate that had to be used to feed the CSTR, was directly connected to the final separation and pressure-reducing units, with the reactor bypassed and the static mixer (7) directly connected to the inhibitor column (12); in this way, through several GC analyses, it was possible to obtain the monomer chromatography peak area corresponding to zero conversion (A_0), which had to be used as a reference to evaluate the MMA conversion and polymerization rate.

Startup

The system was conditioned with CO₂ at the desired flow rate, whereas the reactor was heated to the polymerization temperature. Both filter

units (11), f1 and f2, were pressurized, and GC analyses were made to verify the absence of the solvent from the previous cleaning of the reactor.

At zero time, with the reactor connected to the f1 filter (transient filter), the liquid-chromatography pump (6) was activated to feed the mixture of MMA, surfactant, and AIBN at the desired flow rate. The MMA concentration in the outlet stream was measured by GC every 20 min, and the liquid trapped in the gas–liquid separator (15) was periodically drained.

Stationary Running

When the outlet stream composition was found to be fairly constant (usually after a period corresponding to about three to five mean residence times), the transitory period was considered completed, and the three-way valve (10) was switched to the stationary filter unit (f2) to collect the polymer that formed during the steady-state operation of the reactor. The liquid trapped in the scrubber (15) was periodically drained and stored at a low temperature ($<5\text{ }^{\circ}\text{C}$) for further characterization.

Shutdown

At the end of the experiments, the liquid pump (6) was stopped, the three-way valve (10) was switched to transient filter f1, and the reactor was cooled to room temperature. Hence, liquid CO_2 at 20 MPa was pumped at a flow rate of about 5 mL/min to drag the polymer particles from the reactor to f1, at which the nonreacted monomer, surfactant, and initiator were extracted from poly (methyl methacrylate) (PMMA). After about five mean residence times, the three-way valve (10) was switched to f2 to purify with liquid CO_2 the PMMA synthesized under steady-state conditions. The quantitative removal of MMA was detected by GC analyses. Then, the system was vented, and the polymer was collected from the filter units. After each experiment, the reactor and lines were cleaned with liquid THF, which is a good solvent of PMMA.

Product Characterization

The particle morphology was analyzed and imaged with a Philips scanning electron microscope according to a procedure described elsewhere.⁴¹

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) with an HP 1100 liquid chromatograph equipped with three columns in series (10- μm pack-

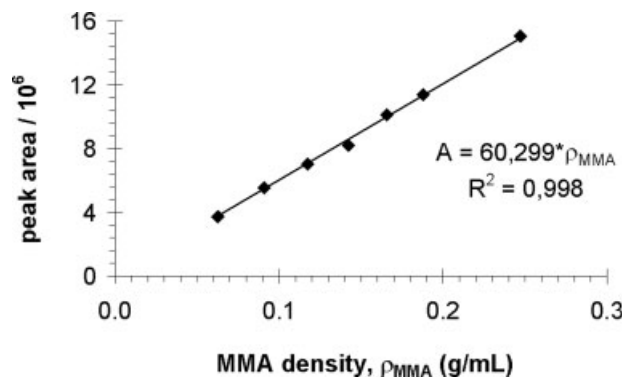


Figure 4. Example of a GC calibration line.

ing and 10^4 -, 10^5 -, and 10^6 -Å porosity) and a refractive-index detector. Monodispersed PMMA standards were used for calibration, and THF was used as an eluent ($35\text{ }^{\circ}\text{C}$, 1 mL/min flow rate, 20- μL injection, and 0.1% w/v PMMA solution).

Infrared spectra were recorded on a PerkinElmer Spectrum 2000 Explorer Fourier transform infrared (FTIR) instrument with an average of 16 scans at a resolution of 1 cm^{-1} with a near-infrared fast-recovery deuterated triglycine sulfate detector. Analyses were performed both on the polymer powder mixed with anhydrous KBr and then compressed to produce solid pellet and on samples of the liquid drained from the gas–liquid separator with a suitable cell with KBr windows.

RESULTS AND DISCUSSION

Flow Model Assessment

Some preliminary tests were made to verify the hypothesis of perfect mixing in the polymerization reactor and to validate the methodology of online sampling and analysis of the high-pressure fluid stream.

In Figure 4, an example of a GC calibration line is reported; it was obtained by the direct pumping of the reaction mixture to the pressure-decreasing section with the reactor and filter units bypassed. Samples of the compressed stream were analyzed by GC to obtain the relationship between the monomer peak areas and MMA density [ρ_{MMA} (g/mL)]. The experiments were carried out at room temperature and $25 \pm 0.3\text{ MPa}$, as these were the conditions of the outlet fluid mixture during the polymerization experiments.

The density of the feed mixture (ρ_m) was evaluated by the Peng–Robinson equation of state,⁴² which describes with good accuracy the phase behavior of the CO_2 –MMA system under the adopted

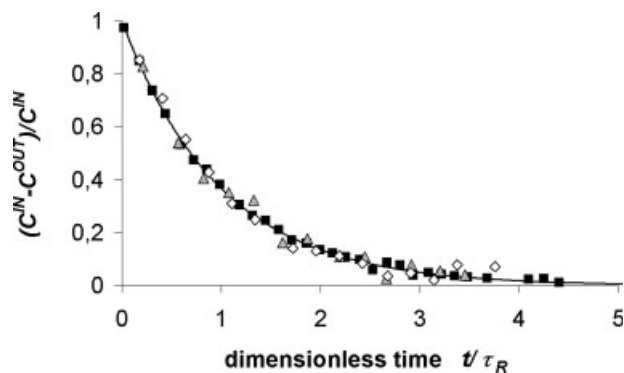


Figure 5. Residence time distribution in the reactor: a comparison of the experimental points and theoretical curves for a perfectly mixed reactor in terms of the adimensional time and concentration (65 °C and 25 MPa): (■) $[MMA]_0 = 0.054$ g/mL with stirring at 500 rpm, (▲) $[MMA]_0 = 0.071$ g/mL with stirring at 800 rpm, and (◇) $[MMA]_0 = 0.161$ g/mL with stirring at 800 rpm.

conditions.⁴⁰ Therefore, the volumetric flow rate and the monomer molar concentration (C^{out}) could be easily evaluated from the results of the GC analysis.

To determine if the reactor behaved as an ideal CSTR (i.e., a perfectly mixed reactor), a set of experiments was performed in which pure CO₂ was pumped to the reactor, which was maintained at 65 °C and 25 MPa, with the inhibited monomer as a tracer. A step flow rate of MMA was pumped to the reactor at time zero, and the answer of the system in terms of the monomer outlet concentration as a function of time was recorded by GC.

Different experiments were carried out with changes in the agitation speed (500 and 800 rpm), feed composition, and flow rates. For an ideal CSTR, the following relationship between the inlet tracer concentration (C^{in}), time t , and the outlet tracer concentration (C^{out}) should be valid:

$$C^{out}(t) = C^{in} \left[1 - \exp \left(-\frac{t - t_d}{\tau_R} \right) \right] \quad (1)$$

where τ_R is the mean residence time ($\tau_R = V_R/Q^{in}$, where V_R is the reactor volume and Q^{in} is the volumetric inlet flow rate) and t_d is a delay time due to the presence of capacities placed both upstream and downstream of the reactor (e.g., the filter units).

As shown in Figure 5, experimental points can be excellently fitted by this equation, and a steady-state condition (i.e., $C^{out} \approx C^{in}$) was achieved after a time period corresponding to three to five mean residence times.

According to these results, we can consider the reactor perfectly mixed for species molecularly dissolved in the medium (e.g., MMA in scCO₂). On the other hand, polymerizations in scCO₂ are heterogeneous processes, and solid particles are dispersed in the reactor. With our experimental setup, it is not possible to check if the reactor is well mixed also with respect to the PMMA particles, as this information can be obtained by the measurement of the particle residence time distribution, which is uneasy for such a high-pressure system. On the other hand, because the swollen PMMA particles have sizes in the micrometer range and a density not too different from that of the dispersing medium (the density of PMMA is ca. 1.1 g/mL), it seems reasonable to assume that the reactor is perfectly mixed also with respect to them.

Continuous Polymerization of MMA

The assembled polymerization apparatus was used to carry out some experiments at different mean residence times with changes in the flow rate of the reaction mixture, whereas all other process parameters were kept constant. The operative conditions adopted for this set of experiments are summarized in Table 1.

Under the adopted conditions, the density of the feed mixture was estimated by the Peng–Robinson equation of state to be 0.87 g/mL; the effect of the surfactant and initiator on the phase behavior of the CO₂/MMA mixture was neglected in this calculation.

The polymer was collected from the filter units in the form of a white powder.

Table 1. Continuous Polymerization of MMA: Experimental Conditions^a

Entry	Feed Molar Flow Rates (mol/h)		Q_{feed} (mL/min)	τ_R (min)
	MMA	CO ₂		
1	0.40	2.53	2.90	35
2	0.23	1.44	1.65	61
3	0.13	0.82	0.94	107
4	0.10	0.60	0.69	145

^a The feed composition was 5 wt % surfactant Sb1784 with respect to MMA and 0.66 wt % initiator AIBN with respect to MMA. The temperature was 65 °C, the pressure was 25 MPa, and the stirring “speed” was 800 rpm. $\tau_R = V_R/Q_{feed}$, where τ_R is the mean residence time, V_R is the reactor volume (100 mL), and Q_{feed} is the volumetric flow rate to the reactor.

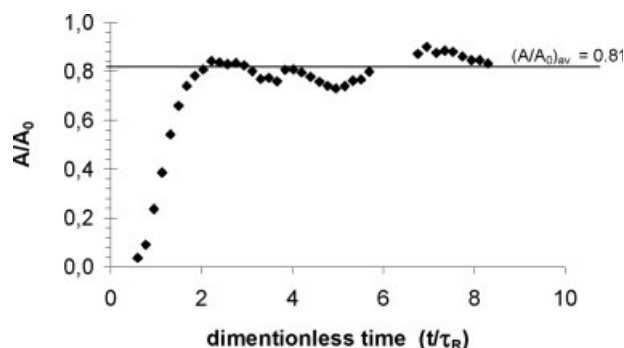


Figure 6. Example of a conversion profile from GC online analyses.

Because the GC calibration line shows that MMA peak areas (A) are proportional to the monomer density (ρ_{MMA} ; Fig. 4), if A and A_0 are the peak areas corresponding to the MMA gravimetric flow rate in the outlet ($M_{\text{MMA}}^{\text{out}}$) and feed streams ($M_{\text{MMA}}^{\text{in}}$), respectively, it is possible to approximate the monomer conversion (X) as a function of the peak areas as follows under the assumption of a constant volumetric flow rate:

$$X = 1 - \frac{\rho_{\text{MMA}}^{\text{out}}}{\rho_{\text{MMA}}^{\text{in}}} = 1 - \frac{A}{A_0} = 1 - \frac{M_{\text{MMA}}^{\text{out}}}{M_{\text{MMA}}^{\text{in}}} = X^{\text{GC}} \quad (2)$$

The hypothesis of a constant volumetric flow rate can seem particularly restrictive because a supercritical fluid is by definition a compressible solvent. Anyway, the technique adopted to measure conversions by GC X^{GC} implies sampling of liquid streams, so it can be considered rather well approximated.

We must consider that eq 2 is rigorously exact only in the case of negligible monomer sorption in the polymer particles. On the other hand, it has been proved by swelling measurements that MMA dissolves in its polymer in scCO_2 even if quantitative data are not available.⁴³ For this reason, GC conversion can be considered only an estimation under the adopted experimental setup.

Figure 6 shows a typical trend of A/A_0 as a function of the adimensional time t/τ_R ; in all the experiments, steady-state conditions were reached after a time interval corresponding to two to three mean residence times.

A fluctuation of the conversion estimated by GC under nominal steady-state conditions can be observed in Figure 6; this behavior has often been described in the continuous emulsion polymerizations of different vinyl monomers in unseeded CSTRs^{44,45} and has been attributed to the effect of periodic polymer particle generations.^{44,46} It has been shown that these fluctua-

tions can be eliminated if the reactor is fed with seed particles or, equivalently, a tubular prereactor is placed in which the polymerization and nucleation of polymer particles can be initiated.⁴⁷

The monomer conversion was determined from the average values of both A and A_0 , which were obtained with a large enough number of GC injections after steady-state attainment (Fig. 6). Because the amount of the monomer that impregnates the polymer particles in the filter units is not taken into account, X^{GC} is higher than the real conversion (X). To consider the effect of the monomer dissolved in the polymer particles, X was computed (Table 2) via the weighing of the amount of the dry polymer collected from the steady-state filter after it was washed with dense CO_2 (W_p) and the mass of the monomer (W_{MMA}) pumped during the stationary running period (9). The relationship between the two different conversions can be obtained from the mass balance equations of the monomer written as a function of the two different parameters:

$$M_{\text{MMA}}^{\text{in}} = (1 - X^{\text{GC}})M_{\text{MMA}}^{\text{in}} + V_r R_p + \alpha X M_{\text{MMA}}^{\text{in}} \quad (3)$$

$$V_r R_p \vartheta = W_f = X M_{\text{MMA}}^{\text{in}} \vartheta = X W_{\text{MMA}} \quad (4)$$

where $M_{\text{MMA}}^{\text{in}}$ is the inlet weight flow rate of the monomer (g s^{-1}), V_r is the reactor volume (mL), R_p is the polymerization rate ($\text{g s}^{-1} \text{mL}^{-1}$), and α is the monomer sorption ($\text{g of MMA/g of polymer}$).

Solving both equations with respect to $V_r R_p$ and considering that

$$M_{\text{MMA}}^{\text{in}} = \frac{W_{\text{MMA}}}{\vartheta} \quad (5)$$

we can relate the two different conversions with the following equation:

$$X = \frac{1}{(1 + \alpha)} X^{\text{GC}} \quad (6)$$

Table 2. Effect of the Mean Residence Time on the Continuous Dispersion Polymerization of MMA in scCO_2 ^a

Entry	τ_R (min)	X^{GC} (%)	X (%)
1	35	13	8
2	61	19	13
3	107	27	18
4	145	31	26

^a τ_R = mean residence time; X^{GC} = MMA conversion determined by GC analysis; X = MMA conversion determined from the amount of the polymer collected from the steady-state filter unit.

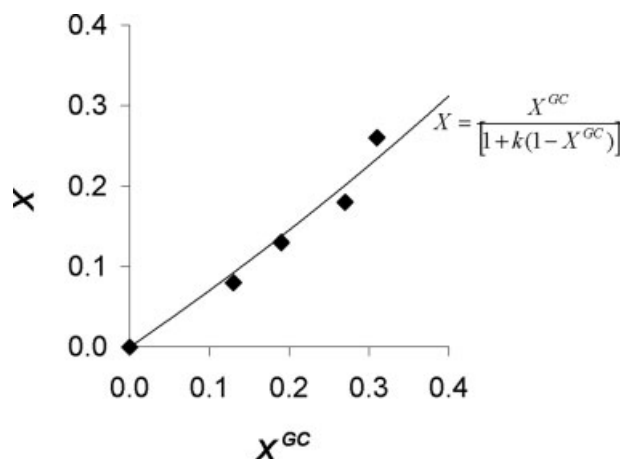


Figure 7. Comparison of the conversion estimated by GC (X^{GC}) and the conversion computed gravimetrically by the weighing of the dry polymer produced during the steady state (X).

If, on a first approximation, we assume that partition coefficient of the monomer between the polymer and the fluid phase does not depend on the MMA concentration in the liquid stream, we can relate α to X^{GC} by the following equation:

$$\alpha = \frac{\gamma}{\rho_p} \frac{M_{MMA}^{in}}{Q} (1 - X^{GC}) \quad (7)$$

where $\gamma = C_{MMA}^p / C_{MMA}^f$ is the partitioning coefficient expressed as a function of the ratio of the monomer molar concentrations in the polymer (C_{MMA}^p) and in the fluid phase (C_{MMA}^f); ρ_p is the polymer density; and Q is the volumetric flow rate of the liquid mixture in the sampling loop, which is assumed to be equal to the inlet volumetric flow rate. Under the adopted experimental conditions, both the polymer density and the M_{MMA}^{in}/Q ratio can be considered roughly constant, and eq 6 can be rewritten as follows:

$$X = \frac{X^{GC}}{1 + k(1 - X^{GC})} \quad (8)$$

where

$$k = \frac{\gamma}{\rho_p} \frac{M_{MMA}^{in}}{Q}$$

Experimental data for the gravimetric and GC-determined conversions are presented in Figure 7, and they have been fitted quite well with eq 8, assuming a value of 0.47 for parameter k .

Once the value of k is determined, R_p also can be estimated from GC analyses with eq 9:

$$R_p = \frac{M_{MMA}^{in}}{V_r} \frac{X^{GC}}{1 + k(1 - X^{GC})} \quad (9)$$

The values of R_p have been plotted as a function of the mean residence time in Figure 8; it can be clearly observed that the higher the residence time and therefore the monomer conversion are, the lower the steady-state value is of the polymerization rate.

For comparison, in Figure 9 are plotted the conversion profiles obtained from the batch polymerization of MMA carried out under operative conditions similar to those adopted in the CSTR. Batch experiments were performed in a 28-mL constant-volume reactor with an experimental apparatus and procedure elsewhere described;⁴¹ as a surfactant, a reactive polysiloxane macromonomer (PDMS monomethacrylate; number-average molecular weight = 10,000 g/mol; supplied by Aldrich) was used that was quite similar to Sb1784. Three different profiles are reported; the initial concentrations of the monomer, initiator (AIBN), and PDMS surfactant were kept constant in all the experiments, whereas the polymerization time (computed since the attainment of the setup temperature of 65 °C) was changed. Each profile was obtained with a different amount of CO₂ loaded in the reactor, which led to different values of the initial pressure (24, 29, and 34 MPa). We observed that, under the adopted experimental conditions, the density of the polymerization medium did not significantly affect the polymerization kinetics (Fig. 9). From the slope of the conversion profiles, it was possible to estimate the instant polymerization rate (R_p^{batch}) and correlate this value with the actual monomer concentration computed from the value of the cumulative

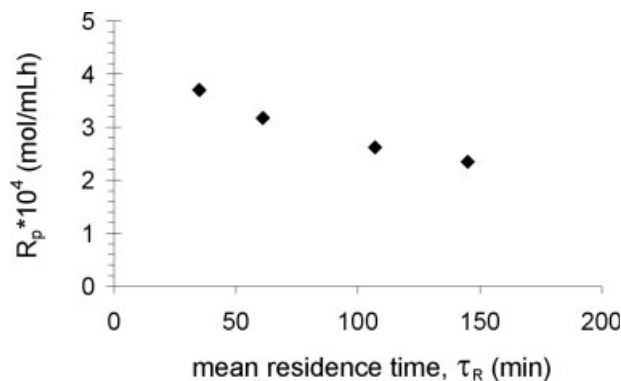


Figure 8. Continuous polymerization of MMA in scCO₂: the polymerization rate (R_p).

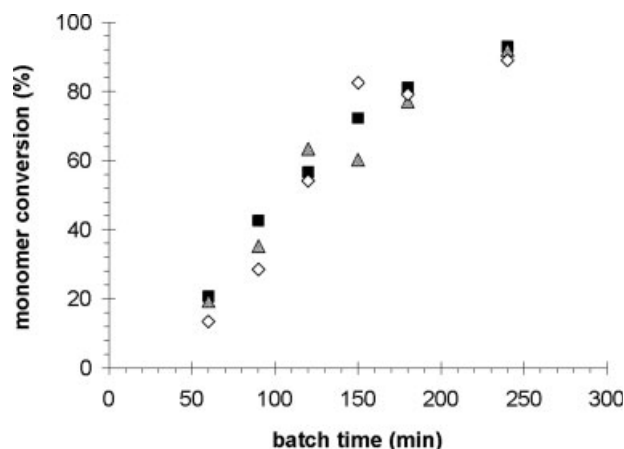


Figure 9. Conversion profiles in the batch polymerization of MMA in scCO_2 [feed: initial monomer concentration = 0.23 g/mL; initial initiator concentration = 0.76 mg/mL; surfactant (reactive PDMS monomethacrylate) concentration = 5 wt % with respect to the monomer; temperature = 65 °C; reactor volume = 28 mL] The initial pressure (at 65 °C) was (■) 24, (▲) 29, or (◇) 34 MPa.

conversion. Because of an autoacceleration effect, R_p^{batch} increased up to $3\text{--}10 \times 10^{-4} \text{ mol mL}^{-1} \text{ h}^{-1}$ of MMA consumption in the time interval of 0–150 min, when the actual monomer concentrations were quite close to those attained for the continuous process under steady-state conditions (i.e., 1.9–2.3 mol/L). Hence, the values of R_p^{batch} determined in batch experiments can be considered to be in good agreement with those determined with the continuous apparatus, which were in the $2\text{--}4 \times 10^{-4} \text{ mol mL}^{-1} \text{ h}^{-1}$ range (Fig. 8).

Even after a prolonged cleaning of the reactor with compressed liquid CO_2 , a significant amount of PMMA was found after the evaporation of the THF that was used to definitely wash the CSTR. To obtain an explanation of the origin of this polymer after a polymerization run, the reactor was opened at the end of the washing with liquid CO_2 . We observed that the inner wall of the reactor was covered with a solid polymer layer (thickness < 1 mm), whose molecular weight was analyzed by GPC and was considerably lower than that of PMMA collected in the steady-state filter units. The formation of polymer films inside a stirred reactor used to carry out the dispersion polymerization of MMA in scCO_2 has already been described in the literature.⁴⁸ This film was hypothesized to have originated from the premature termination of macroradicals on the stainless steel surface of the reactor, and it was found that complete coverage of the metal surface with a stable layer was essential to

obtain high polymer yields. As THF is a good solvent of the polymer, with the cleaning procedure usually adopted in this study, the layer was dissolved at the end of each polymerization and then collected after solvent evaporation.

The main technical drawback that occurred during the polymerization experiments was the obstruction of the reactor outlet tube (Fig. 3), which was particularly frequent in the longer experiments as a result of polymer particle deposition in the tube collecting the outlet stream from the reactor. This was, for example, the case for the experiment with the largest mean residence time, which had to be repeated several times to have a steady-state interval long enough to determine the monomer conversion (entry 4). This phenomenon could be better controlled by the widening of all the outlet lines to the filter units and/or the use of a surfactant with higher interfacial activity to reduce the number of polymer particles sticking to the tube walls.

Product Morphology and Molecular Weight

The polymer collected from the filter units was analyzed with scanning electron microscopy (SEM), and it was composed of microspheres with different particle size distributions at different mean residence times. Two micrographs with the relative size distributions are shown in Figure 10(a,b). Figure 11 reports the particle size distribution obtained in a batch polymerization carried out with an initial polymerization recipe similar to that adopted for the continuous run. The polymer particles produced in the CSTR had larger diameters than those produced in the batch process.^{29,39,49} Indeed, although the number-average diameters attained with the continuous process were always larger than 3.7 μm , in batch processes, under similar operative conditions, number-average particle diameters lower than 2.6 μm were measured despite a larger monomer conversion (the final monomer conversion in the batch polymerizations was higher than 90%). The differences between batch reactors and unseeded CSTRs can be attributed to the polymer particle nucleation and stabilization mechanisms. As the adopted surfactant is a reactive macromonomer, the steric stabilization of the polymer latex depends on the concentration of grafts available in the continuous medium and on their rate of generation in comparison with the rate of growth of the polymeric interface. In batch reactors, the nucleation period is considered completed at low conversion levels (<0.1%) when the rate of graft formation is high, and for this reason a large number of particles can

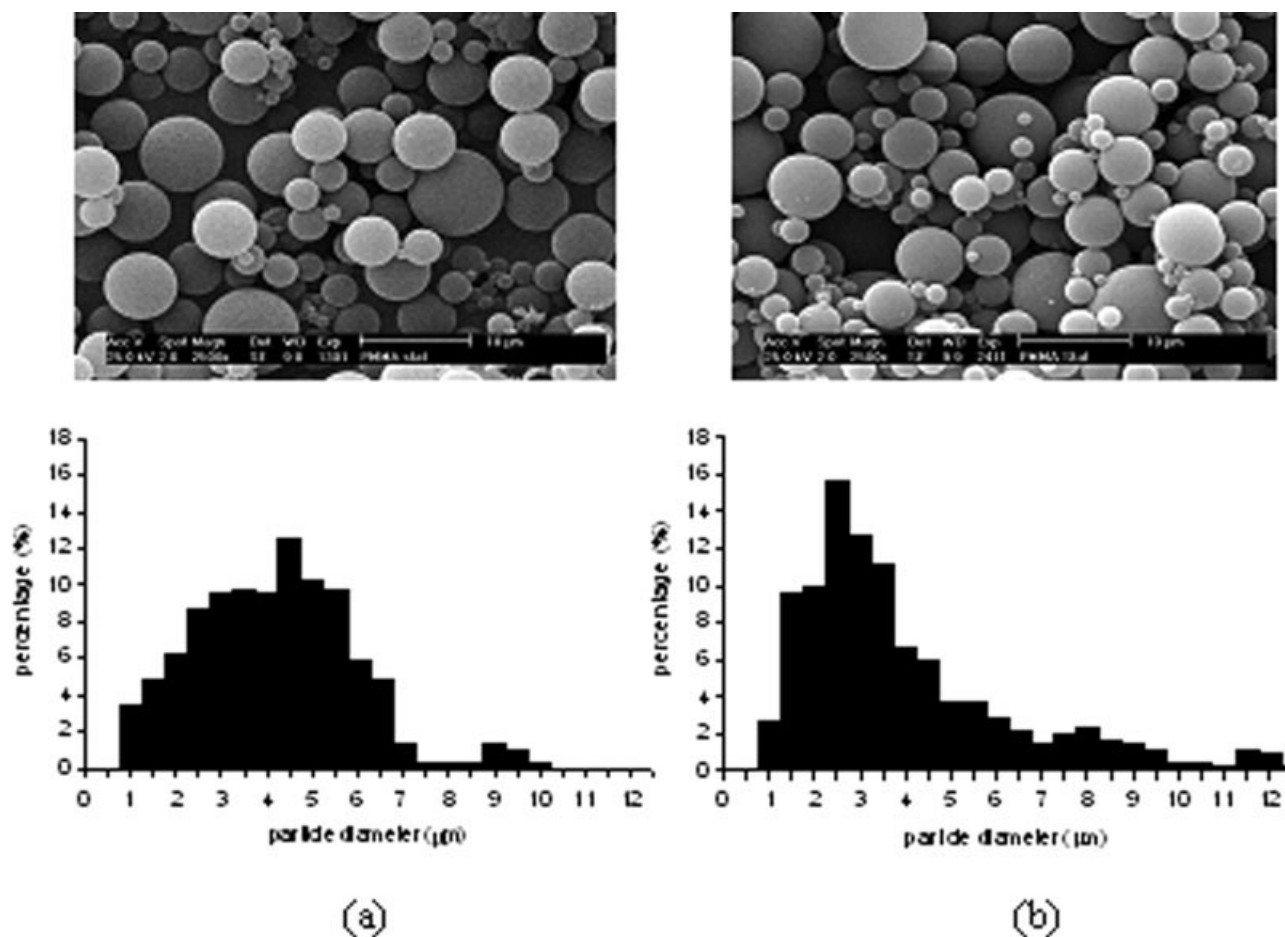


Figure 10. Continuous polymerization of MMA in scCO_2 : SEM images and particle size distributions of PMMA powder produced at mean residence times of (a) 35 and (b) 107 min.

be stabilized by the relatively high concentration of grafts available in the continuous medium. As a result, at the end of the nucleation period, the small polymer particles will be surface-saturated with the whole emulsifier present in the system and will be able to grow until the end of the reaction, while the particle number will remain constant. On the other hand, in an unseeded steady-state CSTR, a fraction of the grafts generated inside the reactor is needed to support the continuous nucleation process, and consequently, the effluent will be characterized by larger particles saturated by a smaller amount of the *in situ* generated emulsifier.

These different conditions, together with the larger residence time distribution for the particles, may justify the wider particle size distribution of the product from the CSTR compared with that obtained in batch processes.^{29,39,49} When high mean residence times were adopted, the particle size distribution broadened, and bimodality became more evident; the number-average particle diameters

remained quite constant (ca. $3.8 \mu\text{m}$), and the weight-average particle diameters increased with the mean residence time, probably because of aggregation of smaller particles, as confirmed by SEM analyses, which showed that smaller particles in the powder often stuck to one another or collapsed onto the surface of larger particles.

In Table 3, the results obtained from GPC analyses of PMMA powders recovered from the filter units under steady-state conditions are reported.

Similarly to the particle size distributions, the molecular weight distributions were found to be wider than those obtained in batch processes;^{29,39,49} then again, the broadening of the polymer property distribution could be attributed to the larger mean residence time distribution typical of continuously mixed reactors. In addition, we found a reduction of the polydispersity index (weight-average molecular weight/number-average molecular weight) when the monomer conversion increased (i.e., when the mean residence time was increased).

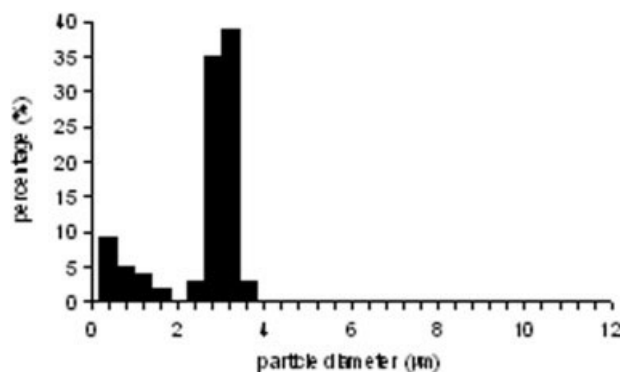
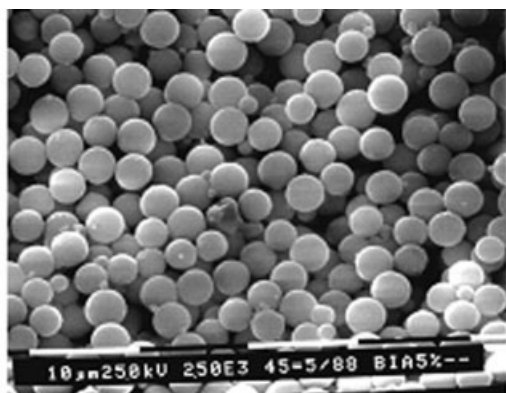


Figure 11. SEM image and particle size distribution of PMMA powder produced in scCO_2 in a batch reactor with a process recipe similar to that adopted in the continuous polymerization.

Distribution of the Surfactant between the Polymer and the Outlet Liquid Stream

The surfactant content of the synthesized polymer and the liquid drained from the reaction system during the experiments was studied with FTIR spectroscopy to investigate the mechanism of stabilization of the PDMS macromonomer stabilizer

Table 3. Effect of the Mean Residence Time on the Molecular Weight of the Polymer Synthesized in the Continuous Dispersion Polymerization of MMA in scCO_2 ^a

Entry	τ_R (min)	X^{GC} (%)	M_w (kg/mol)	M_w/M_n
1	35	13	144	12.2
2	61	19	115	9.8
3	107	27	276	7.9
4	145	31	629	7.1

^a τ_R = mean residence time; X^{GC} = MMA conversion determined by GC analysis; M_w = weight-average molecular weight; M_n = number-average molecular weight; M_w/M_n = polydispersity index of the molecular weight distribution.

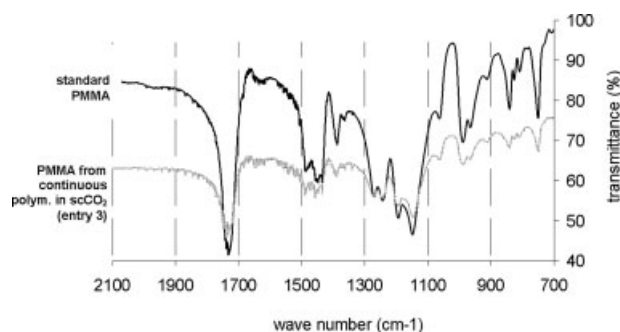


Figure 12. FTIR analysis: a comparison of PMMA synthesized in scCO_2 and a commercial sample.

and to evaluate the possibility of its recovery and recycling to the reactor. This is a particularly important issue for the utilization of the apparatus because of the relatively large amount of the surfactant that must be used for the polymerization experiments (7–12 g for each experimental run).

In Figure 12, a PMMA sample synthesized in the CSTR (entry 3) is compared with a commercial sample of the polyacrylate: the two spectra seem to be equivalent, and no evidence of the absorption bands of PDMS, at about 1000–1100 ($\text{Si}-\text{O}-\text{Si}$ bonds) and 810 cm^{-1} ($\text{Si}-\text{CH}_3$ bonds), can be detected in the sample synthesized in scCO_2 .

Also, the liquid solution that was drained during the polymerizations was analyzed with FTIR spectroscopy. Three different liquid samples were compared, all of them diluted in cyclohexane at the same nominal concentration:

1. Liquid that was drained during a polymerization run (entry 3).

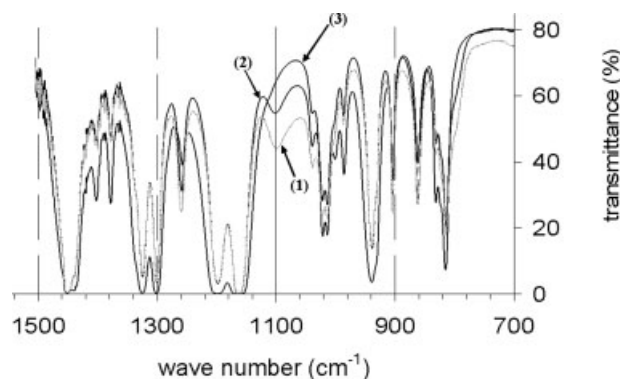


Figure 13. FTIR analysis: a comparison of (1) an outlet liquid solution drained during polymerization in the steady state (entry 3), (2) a feed mixture (MMA and 5 wt % PDMS), and (3) a pure monomer (MMA). All mixtures were equally diluted in cyclohexane.

2. Feed mixture (solution of MMA with 5 wt % Sb1784 PDMS macromonomer).
3. Pure MMA.

The three corresponding FTIR spectra can be compared in Figure 13: they appeared equivalent with the exception of a large peak at about 1100 cm^{-1} , which could be attributed to the presence of the siloxane surfactant. We compared the ratio of the absorbance of this band to that of the band at 940 cm^{-1} , which could be attributed to the out-of-plane C—H bending of the alkene, for the drained liquid and the feed mixture. With this comparison, we computed a marked increase in the concentration of the stabilizer in the drained liquid (computed value = 2.3). On the basis of these results, it seems reasonable to conclude that a significant number of PDMS chains were recovered with the nonreacted monomer. Then, the possibility of recycling the surfactant and the monomer to the reactor may be considered. In this respect, it is interesting to observe that the fluid phase to be recirculated is a liquid mixture,⁴⁰ almost at the same pressure of the reactor, and therefore a limited energetic cost for the recycling could be expected. This practice can reduce the impact of the surfactant cost on the economics of the process and increase the quality of the product in terms of purity.

CONCLUSIONS

A laboratory-scale apparatus for the continuous polymerization of vinyl monomers in scCO_2 was assembled, and its functionality was tested through the free-radical dispersion polymerization of MMA in the presence of a PDMS macromonomer surfactant.

Considerable research effort was dedicated to the design, setup, and gradual amelioration of the apparatus and experimental protocol. The dispersion free-radical polymerization of vinyl monomers was performed continuously to cumulate the advantages offered by the presence of a surfactant with those arising from the adoption of continuous processes. Under the adopted conditions, when the mean residence time was increased from 35 to 145 min, the MMA conversion increased from 8 to 26% with a polymerization rate in the range of $2\text{--}4 \times 10^{-4}\text{ mol mL}^{-1}\text{ h}^{-1}$.

PMMA was collected in the form of a white powder composed of microspheres with diameters in the range of $1\text{--}10\text{ }\mu\text{m}$ and weight-average molecular weights (GPC) in the range of $100\text{--}700\text{ kg/mol}$; both the particle size and molecular weight distributions

were larger than those obtainable in batch processes with similar process recipes and conditions.

FTIR analyses of the synthesized polymer and liquid drained from the reaction system suggested that an almost quantitative recovery of the surfactant from the polymer could be obtained, with potential positive implications for the process economy and product quality.

The main drawback to overcome was the occurrence of system blockages due to polymer particle deposition in outlet piping and pressure-decreasing valves, which was found to be more frequent with increasing solid content in the effluent stream from the CSTR. This phenomenon could be better controlled by the widening of all the outlet lines to the filter units and/or the use of a surfactant with higher interfacial activity to prevent polymer particles from sticking to the tube walls.

Another important issue that in our opinion must be better analyzed is internal reactor agitation, which can be properly controlled to ensure that a good mixing level is reached also for solid particles.

We emphasize that the laboratory-scale plant configuration described here can be easily adapted, just with minor changes, to the heterogeneous free-radical polymerization and copolymerization of different monomers, as well as other reactions in scCO_2 -based media both homogeneously and heterogeneously catalyzed.

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