

CONTINUOUS DISPERSION POLYMERIZATION OF METHYL METHACRYLATE IN $scCO_2$

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ABSTRACT: the set up of a lab-scale plant for continuous heterogeneous polymerization in supercritical carbon dioxide ($scCO_2$) is presented. The objective of this work is to study the polymerization kinetics, particle nucleation mechanisms and to evaluate the possibility of in-situ product purification. The dispersion polymerization of methylmethacrylate (MMA) in $scCO_2$ in the presence of a polysiloxane macromonomer surfactant and 2,2'-azobisisobutyronitrile (AIBN) as initiator has been carried out with this equipment. We report the results of preliminary tests concerning the effects of mean residence time on monomer conversion, polymerization rate and particle size distribution.

INTRODUCTION

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

While organic monomers are soluble in $scCO_2$, most polymers are insoluble in this medium: only amorphous fluoropolymers, silicones and polycarbonate-polyether copolymers [2,3] exhibit good solubility in CO_2 under relatively mild conditions ($T < 100^\circ C$, $P < 35$ MPa).

Consequently dispersion and precipitation polymerization techniques are generally adopted and these heterogeneous polymerizations have been mainly investigated in batch processes [4-10].

Nevertheless this, continuous processes lead to many benefits over batch processes. First, they require smaller volumes and then cheaper equipment for equivalent polymer yields; in addition the use of smaller reactors is an advantage for a safer control of the process.

Furthermore, continuous polymer removal from the system enhances a quick quenching and the extraction of monomer and additives (for example a surfactant), facilitating their recycling.

Last but not least, the possibility of making several polymerization runs without opening the reactor avoids the necessity of performing time consuming leak tests before each run.

To our knowledge, the only examples of continuous processes in $scCO_2$ deals with the precipitation polymerization of vinylidene fluoride [11,12].

On the other hand dispersion polymerization allows a better control of the final product as thanks to the presence of a suitable surfactant that stabilizes polymer particles throughout the process high molecular weight polymers can be synthesised in $scCO_2$ under the form of microspherical particles with a narrow size distribution [4-10].

Our research aim is to investigate the utilization of a CSTR for heterogeneous free radical dispersion polymerizations in $scCO_2$. Here we present the utilization of this device for the dispersion polymerization of methylmethacrylate (MMA), widely investigated in batch processes in the presence of a polysiloxane surfactant.

This method may be applied to the polymerizations and copolymerizations of other monomers, in continuous or semi-batch processes, as well used to perform seed polymerization processes in $scCO_2$.

MATERIALS AND METHODS

- *Materials*

Methyl methacrylate (MMA, Aldrich), with purity higher than 99%, was distilled under vacuum at about 50°C to remove inhibitor before use. Poly(dimethylsiloxane) with two methacrylate reactive ends (PDMS, Degussa, type Sb1784, $n = 260$, $M_n = 20,000$ g/mole), was kindly supplied from Degussa and used as received.

2,2'-azobis(isobutyronitrile) (AIBN, Fluka), with purity higher than 98% was stored at low temperature (ca. -4°C) to prevent decomposition.

CO₂ (Sol 99.998 pure), tetrahydrofuran (THF, Lab-Scan HPLC grade) and Hydroquinone (Carlo Erba), were used as received.

- *Apparatus*

A schematic representation of the polymerization apparatus is shown in Figure 1.

It consists basically of a continuous reactor (100 cm³) (1) equipped with a magnetic stirred head type, and with temperature and pressure sensors.

Liquid CO₂ is pressurized with an air-driven pump (Maximator) (2) up to the desired pressure, regulated through a pressure reducer (Tescom) (3). Liquid monomer, surfactant and initiator are pumped at the desired flow rate with a liquid chromatography pump (Gilson) (6). Check valves (4) are placed in this section to prevent backflows.

Both liquid streams (CO₂ and the monomer mixture) are mixed in a high pressure static mixer (7) and then fed to the reactor at room temperature and process pressure.

The temperature of the reactor is controlled with an automatic control system (8) that manipulates the temperature of the water (9) circulating in the reactor jacket.

Since a heterogeneous polymerization takes place, the outlet stream consists of polymer particles dispersed in a CO₂ rich continuous phase. It's cooled down to room temperature and through a 3-way ball valve (10) is sent to one of two jacketed filter units (Headline) (11) for quantitative removal of the polymer particles. To quench the mixture both filter units are maintained at low temperature with cold water circulation in the jackets of the filter housings.

The compressed fluid living the filters is liquid CO₂ with dissolved non reacted monomer, surfactant and initiator. It's passed through a column (12) packed with inhibitor (hydroquinone) to prevent polymerization in the downstream lines and valves. This dense fluid can be sampled with a Rheodyne 2-ways switching valve (13) for on-line GC analysis.

Finally, two different expansion stages (14) allow quasi quantitative separation of CO₂ from the other components of the outlet stream, so that CO₂ flow rate measurements may be achieved downstream and non reacted monomer collected from gas-liquid scrubbers (15).

- *Procedures*

The whole line is initially pressurized with liquid CO₂ flowing at the desired flow rate to fill the apparatus. In the mean time the reactor is heated to the polymerization temperature.

Both filter units (11), f1 and f2, are pressurized, and reactor outlet stream is flowed through one of them (f1).

At time zero liquid pump (6) is activated so that monomer liquid mixture starts to be fed.

The composition of the outlet stream is determined through on-line GC analyses made approximately every 20 min. The liquid trapped in the gas-liquid scrubbers (15) is periodically drained out.

When the outlet stream composition is found to be constant, the start up period is considered completed and the 3-way valve (10) is switched to collect in the filter unit (f2) all the polymer formed during the reactor stationary running.

At the end of process the liquid pump (6) is stopped, 3-way valve (10) switched to filter f1 and reactor cooled down to room temperature: therefore liquid CO₂ entrains the polymer particles suspended inside the reactor (this polymer is trapped in filter f1) and extract non reacted monomer, surfactant and initiator from the polymer collected in both filter units.

Liquid CO₂ is passed until no evidence of monomer in the outlet flow is observed from GC analysis.

Lastly the apparatus is vented and polymer collected from the filter units.

After each experiment reactor and lines are washed with THF to get rid of residual polymer.

- *Particle morphologies* were analyzed and imaged with a Philips scanning electron microscope (SEM). Samples were sputter coated with gold before analysis. The particle size distributions were evaluated by measuring at least 300 individual particles in different sample regions using a software for image analysis of micrographs, then the number-average particle size and particle size distributions were determined.

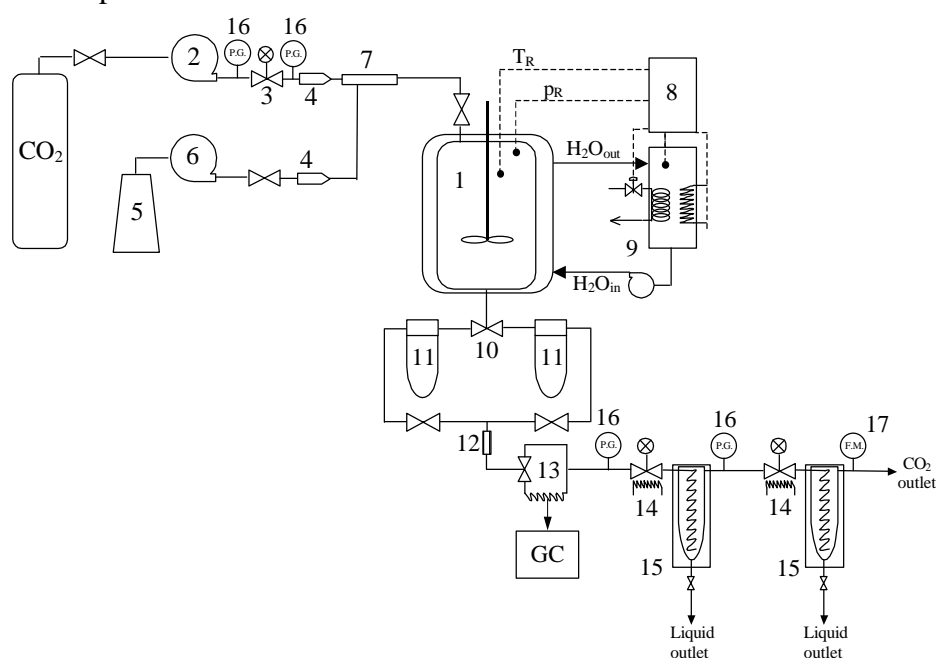


Figure 1: Apparatus for continuous heterogeneous polymerizations. polymerization reactor (1); CO₂ pump (2); pressure reducer (3); check valve (4); liquid reactant mixture (5); liquid pump (6); static mixer (7); interface for reactor temperature control (8); water circulation system for reactor temperature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

RESULTS AND DISCUSSION

A set of experiments was carried out changing the mean residence time inside the reactor (τ_R), varying the feed flow rates. Other process parameters like feed composition, reactor agitation, temperature and pressure were maintained constant.

The experimental conditions are summarized in Table 1. Under these operative conditions, the density of the feed mixture is 0.87 g/mL, estimated using the Peng-Robinson equation of state [13].

Table 1: Continuous polymerisation of MMA: experimental conditions.

Entry	Feed molar flow rates (mol/h)		Feed flow rate Q_{feed} (mL/min)	Estimated mean residence time τ_R (min)
	F_{MMA}	F_{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

mean residence time = $\tau_R = V_R/Q_{\text{feed}}$.

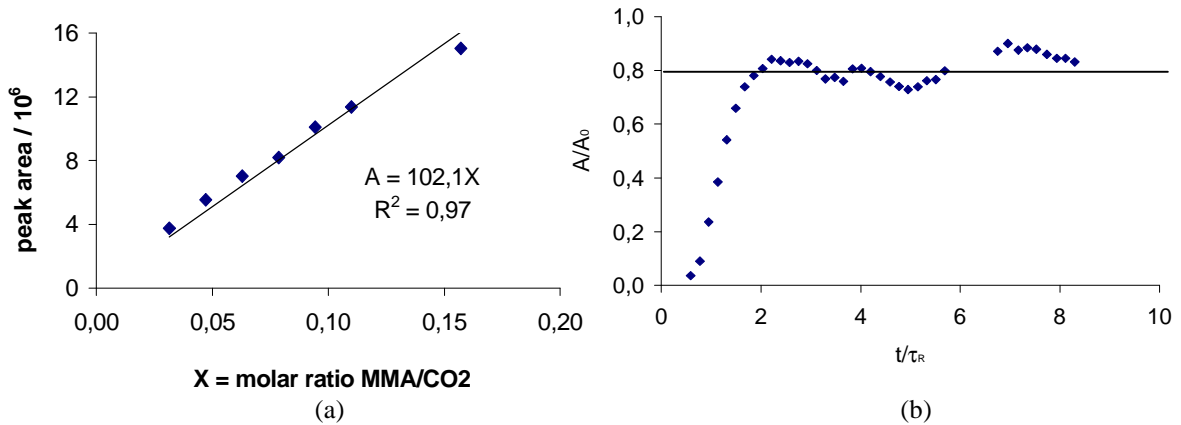
Feed: surfactant = PDMS (Tegomer Sb1784), at 5 wt.% with respect to MMA;
 initiator: AIBN, at 0.66 wt.% with respect to MMA; $X^{\text{IN}} = \text{MMA}/\text{CO}_2 = 0.160$ mol/mol.

Reactor: volume: 100 cm^3 ; $T = 65^\circ\text{C}$; $P = 245 \text{ bar}$; agitation: 800 min^{-1} .

The polymer was always collected from the filter units under the form of a white powder. GC calibration showed that MMA peak areas are proportional to $X = \text{MMA}/\text{CO}_2$ molar ratios (Figure 2a). Consequently, if A and A_0 are the peak areas corresponding to MMA in the outlet and feed stream respectively, we can relate the monomer conversion (conv.%) to the peak areas as follows:

$$\text{conv.}\% = \left(1 - \frac{X^{\text{OUT}}}{X^{\text{IN}}}\right) \cdot 100 = \left(1 - \frac{A}{A_0}\right) \cdot 100$$

Figure 2b shows a typical trend of A/A_0 as a function of adimensional time t/τ_R .

**Figure 2:** GC calibration (a) and on-line analysis during a typical experiment (b).

Monomer conversion is then determined from the average values of both A and A_0 , obtained with a large enough number of GC injections during the reactor stationary running. A_0 is determined before start up, when the reactor is by-passed and the reaction mixture is directly injected to GC.

In all experiments the highest standard deviation found for the single A/A_0 values (from the average value) is $\pm 6.4\%$ in terms of monomer conversion.

Also the polymerization rate R_p can be determined from GC analyses as follows:

$$R_p = \frac{(F_{MMA}^{in} - F_{MMA}^{out})}{V_R} = \frac{F_{MMA}^{in} \cdot (conv\%)/100}{V_R}$$

where F_{MMA}^{in} and F_{MMA}^{out} are respectively the molar flow rates of MMA in the feed and in the reactor outlet stream. Due to uncertainty in the values of monomer conversion, also the values of R_p are to be considered affected by small uncertainty. These results are presented in Table 2.

Table 2: Continuous polymerisation of MMA: preliminary results.

Entry	estimated mean residence time τ_R (min)	MMA conversion (%)	$R_p \cdot 10^4$ (mol/cm ³ ·h)	PMMA yield (%)
1	35	13 (18)	5.1 (± 2.6)	8
2	61	19 (N.A.)	4.4 (± 1.5)	N.A.
3	107	27 (36)	3.6 (± 0.8)	18
4	145	31 (47)	3.1 (± 0.6)	39

MMA conversion: determined with on line GC analysis; between brackets is reported the value determined gravimetrically considering the liquid drained out during reactor stationary running; R_p : polymerization rate determined with on line GC analysis; PMMA yield: value determined weighting the polymer collected from the filter unit used to recover the polymer during reactor stationary running; N.A.: not available.

SEM analysis evidenced the presence of PMMA particles as microspheres with different particle size distributions at different mean residence times (Figure 4).

At the higher mean residence times the particle size distribution broadens and bimodality is more evident. While the number average particle diameter remains quite constant, the weight average particle diameter increases, probably due to aggregation of smaller particles. This is confirmed by SEM images showing smaller particles often stuck each other or to the surface of larger particles.

4. CONCLUSIONS

This work shows that dispersion polymerization in scCO₂ can be carried out in a continuous system and can be considered a preliminary step towards the evaluation of the possibility of making synergetic the benefits of the dispersion technique and of continuous operation such as high molecular weights of polymer, small reactors, easy product purification, non-reacted monomer and surfactant recovery and recycling.

Experiments performed up to now have been aimed to optimize the procedures using as a model process the dispersion polymerisation of MMA. In this phase we have started to investigate the effect of the mean residence time on monomer conversion, polymerization rate and particle size distribution.

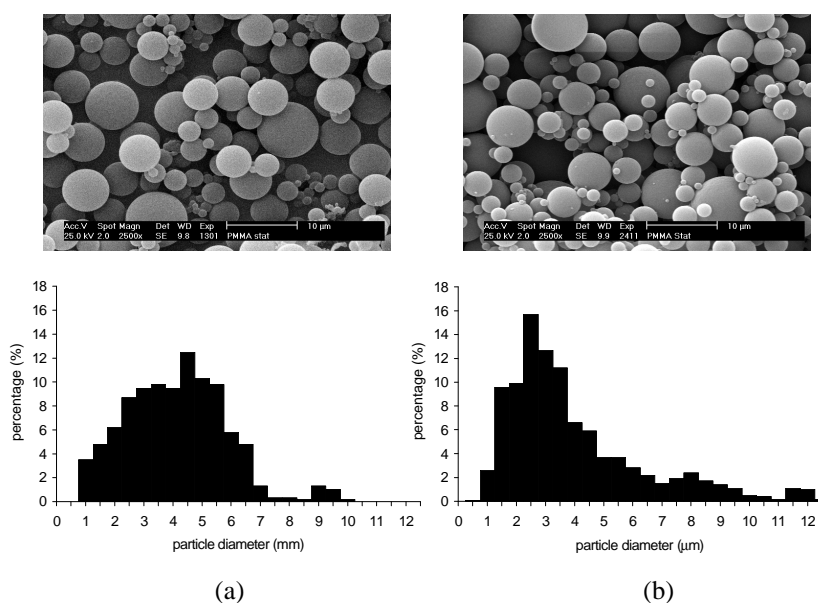


Figure 4: continuous polymerization of MMA: SEM images and particle size distributions of PMMA powder produced at different mean residence times $\tau_R = 35$ min (a) and 107 min (b).

A deeper investigation of the process is going to be done by the characterization of the composition of both polymer product and liquid drained out. This analysis could provide useful information on the mechanism of stabilization and the possibility of surfactant recycle.

ACKNOWLEDGEMENTS

The financial support from GROWTH Project GRD1-2001-40294 is gratefully acknowledged. Authors are grateful to Degussa for the Sb 1784 stabilizer.

5. REFERENCES

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