HETEROGENEOUS POLYMERIZATION OF 1-VINYL-2 PYRROLIDONE IN SC CARBON DIOXIDE IN THE PRESENCE OF REACTIVE POLYDIMETHYLSILOXANE SURFACTANTS

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Batch free radical polymerization of 1-vinyl-2-pyrrolidone (VP) in supercritical carbon dioxide has been studied in the presence of a reactive polysiloxane surfactant (PDMS-mMA). When the initial concentration of the macromonomer is higher than 5% w/w the polymerization process proceeds with a fast kinetics and leads to the formation of spherical nanoparticles with almost quantitative yields (higher than 98%). The effect of the concentration of the surface active macromonomer and initiator AIBN on the morphology of the particles were investigated. A dependence on $[AIBN]^{-0.16}$ of the number average particle diameter was observed exhibiting an exponent quite close to those foreseeable on the basis of Smith-Ewart kinetics for emulsion polymerization.

INTRODUCTION

Dispersion polymerization technique in supercritical CO_2 has been adopted also for the synthesis of water soluble monomers such as 1-vinyl-2-pyrrolidone [1, 2] and glycidyl methacrylate [3] that cannot be synthesized by heterogeneous techniques in water based polymerization systems. Polymer latex has been stabilized by poly(FOA) [2] or diblock stabilizer having a polystyrene block as anchoring portion and PFOA [3] or PDMS [1] as CO_2-philic part. In these processes the formation of sub-micron polymer particles has been reported and the possibility of occurrence of micellar nucleation has been mentioned.

Prompted by these results we have investigated in more details the homopolymerization of 1-vinyl-2-pyrrolidone in the presence of reactive PDMS-mMA as a surfactant in order to test the possibility of using a reactive macromonomer as a stabilizer. The initial concentration of initiator has been varied to obtain indirect information on the nucleation mechanism of polymer particles.

2. MATERIALS AND METHODS

-Polymerization Apparatus Experiments have been carried out in a stainless steel reactor (total volume 32 cm^3) heated by a water bath controlled by a PID based cascade control system. 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.

- *Materials* 1-vinyl-2-pyrrolidone (VP) obtained from Aldrich (99+%), was freshly distilled under vacuum before each test.

2,2'-Azobisisobutyronitrile (AIBN) (Aldrich) and CO_2 (Sol 99.997 pure) were used as received.

Polysiloxane surfactants were supplied by Aldrich (PDMS-mMA) with the following features:

$CH_2=CCH_3-COO-C_3H_6-Si(CH_3)_2-[Si(CH_3)_2O]_nC_4H_9$
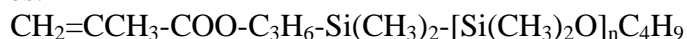
PDMS-mMA (M_n =10000 g/mol, n=130)

Particle morphologies were analysed 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 measuring at least 100 individual particles from the electron micrographs and the number-average particle size and particle size distribution were determined.

Polymer yields were determined gravimetrically.

3. RESULTS AND DISCUSSION

The batch homopolymerization of VP, initiated by the thermal decomposition of AIBN, was carried out in the presence of PDMS-mMA, at fixed concentration of the monomer (20% w/w with respect to CO_2) and roughly constant density (0.9 g/cm^3), by increasing the concentration of the reactive stabilizer from 5 to 12.5 % w/w with respect to the monomer (Table 1). The polymerization process proceeds with a fast kinetics and all reactions were completed in less than two hours as testified by the crossover between the temperature inside the reactor and that of the water bath as a consequence of the vanishing of heat generation from the monomer conversion. Under all adopted experimental conditions yields close to 100% were obtained and the polymer product was collected from the reactor at the end of the experiments in the form of a free flowing powder constituted by sub-micron spherical particles. Figure 1 presents (in a log-log plot) the evolution of the number average particle diameter as a function of the initial surfactant concentration. A slope of –0.78, rather higher than the exponent –0.5 predicted by the model of Paine for grafted stabilizers [4], was computed. To obtain additional information on the mechanism of nucleation we performed a set of experiments by changing the initial concentration of AIBN in a polymerization mixture at 20% w/w VP in the presence of a PDMS-mMA concentration of 5% w/w with respect to the monomer.

**Table 1.** Polymerization of VP in scCO$_2$: effect of the reactive surfactant concentration.

PDMS-mMA, % w/w[a]	P°, MPa	Yield, %	D_n, µm	PSD
12.5	29	98	0.16	1.05
10.0	30	97	0.19	1.04
7.5	28	98	0.26	1.06
5.0	30	99	0.32	1.04

[a]based on the total amount of the monomers.
Reaction system: VP 20% w/w with respect to CO_2, CO_2 added in an amount to reach the density of 0.9 g/cm^3.
AIBN 0.65% w/w based on the monomer. Reaction temperature: T= 65 °C.
P°: initial pressure; D_n: number average diameter; PSD=D_w/D_n: particle size distribution.
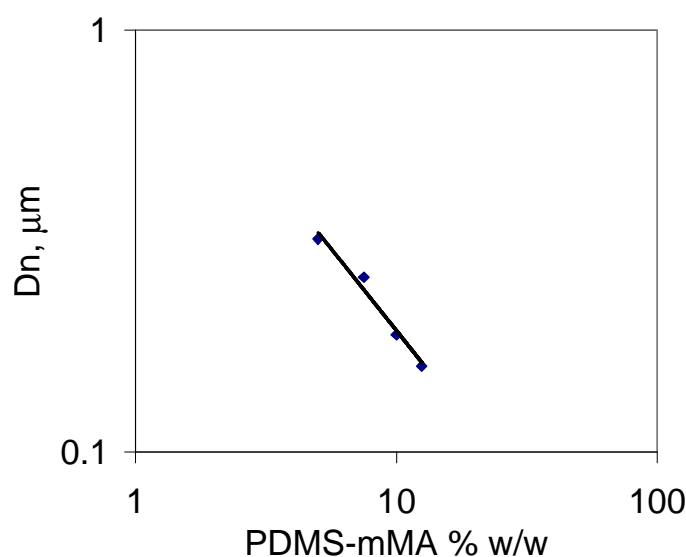
Figure 1. Effect of the initial concentration of the reactive macromonomer on the average diameter of poly(VP) particles synthesised in scCO$_2$.

As reported in Table 2 polymer yields are almost quantitatively and when the initial concentration of AIBN was increased a decrease in particle size was observed according to a scaling relationship (Fig. 2), obtained by least-squares fitting of experimental data, corresponding to $d = k[AIBN]_0^{-0.16}$

Such a negative exponent has a modulus significantly higher than that predicted by the full adsorption model developed by Paine [4] to predict particle size in the case of grafted stabilizers.

Indeed the fitting exponent computed in this study leads to a power law dependence of the particle number on initiator concentration of 0.48 quite close to the 0.40 exponent predicted by the quantitative theory of Smith and Ewart for emulsion polymerization [5].

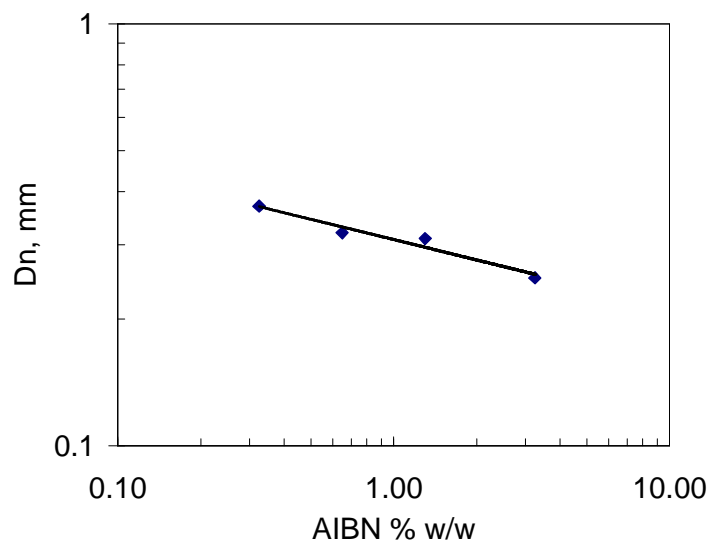**Table 2.** Polymerization of VP in scCO$_2$: effect of the concentration of initiator (AIBN).

AIBN % w/w[a]	P°, MPa	Yield, %	D_n, μm	PSD
0.32	29	99	0.37	1.02
0.65	30	99	0.32	1.04
1.30	28	99	0.31	1.06
3.25	27	99	0.25	1.05

[a]based on the monomer.
Reaction system: VP 20% w/w with respect to CO$_2$, CO$_2$ added in an amount to reach the density of 0.9 g/cm^3.
PDMS-mMA 5% w/w based on the monomer. Reaction temperature: T= 65 °C.
P°: initial pressure; D_n: number average diameter; PSD=D_w/D_n: particle size distribution.

Figure 2. Effect of the initial concentration of the initiator on the average diameter of poly(VP) particles synthesised in $scCO_2$.

4. CONCLUSIONS

Heterogeneous polymerization of VP in the presence of PDMS-mMA in $scCO_2$ exhibits fast kinetics and leads to the formation of polymer under the form of sub-micron particle size with almost quantitative yields. When the initial concentration of the initiator is increased the particle diameter decreases with a scaling law having an exponent higher than that proposed by Paine. This could be explained by postulating a more complex nucleation mechanism of the polymer particles with respect to that assumed in the development of the aforementioned model. To investigate this behavior in deeper detail experiments changing the monomer concentration and the fluid phase density (solvency of the polymerization medium) are going to be performed.

5. REFERENCES

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