

The wall effect: how metal/radical interactions can affect polymerisations in supercritical carbon dioxide

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Abstract

We describe the radical dispersion polymerisation of methyl methacrylate in supercritical carbon dioxide using a poly(dimethylsiloxane) monomethacrylate as the stabiliser. Initial observations showed that in the absence of efficient stirring, acceptable yields, molecular weight and particle morphology for PMMA were observed. However, efficient stirring of the reaction mixture was found to substantially reduce yield and quality of the resulting PMMA. We speculate that this is caused by radical quenching occurring at the metal wall of the reaction vessel during the reaction. By lowering of the initiator concentration it was found that a coating of high molecular weight PMMA was formed on the exposed internal metal surface of the cell. Subsequent experimental studies showed that the coating acts as a barrier to inhibit radical termination and facilitate the polymerisation of MMA with stirring. We show that consideration must be given to the composition of the metal surface of the autoclave, and that by careful choice of reaction conditions, a durable, and impermeable PMMA coating may be deposited within the autoclave. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The use of supercritical carbon dioxide as a polymerisation medium has increased rapidly over the recent past [1]. Supercritical carbon dioxide (scCO₂) offers a number of advantages over conventional solvents, being environmentally clean, relatively cheap and possessing tuneable physical properties [2]. A particularly active area has been the free radical polymerisation of acrylates in scCO₂ by dispersion polymerisation. Some fluorinated and siloxane based polymers exhibit good solubility in scCO₂ and have been shown to be effective stabilisers and surfactants [3–6].

DeSimone et al. have shown that methyl methacrylate (MMA) undergoes dispersion polymerisation in scCO₂ utilising block co-polymer stabilisers where the soluble section is either poly(1,1-dihydroperfluorooctyl acrylate) [FOA] or poly(dimethylsiloxane) [PDMS] [7,8]. Others have developed similar materials [9]. By contrast, Beckman et al. have synthesised a series of graft copolymers,

poly(methyl methacrylate-co-hydroxyethyl methacrylate)-g-poly(perfluoropropyl oxide), which are also effective stabilisers for the dispersion polymerisation of MMA in scCO₂ [10].

An alternative approach is the use of siloxane-based macromonomers (Fig. 1) [PDMS macromonomers] for the dispersion polymerisation of methyl methacrylate in scCO₂ [11–13]. Macromonomers are oligomers or polymers with a polymerisable terminal functional group which are commonly used for the formation of graft copolymers [14]. The drawback to the use of such materials is that they are necessarily incorporated into the PMMA polymer. The amount of PDMS macromonomer in the final polymer is however very low (typically less than 0.25 wt.% in the PMMA for a 7 wt.% PDMS macromonomer feed) [13,15].

In a research program targeted at developing novel stabilisers for free radical polymerisation in scCO₂, we began by investigating the use of a commercially available methacryloxy functional PDMS macromonomer as a stabiliser for polymerisation of methyl methacrylate. Surprisingly, these results demonstrate that the condition of the internal metal surface of the autoclave is critical in determining the yield, molecular weight and morphology of the PMMA produced.

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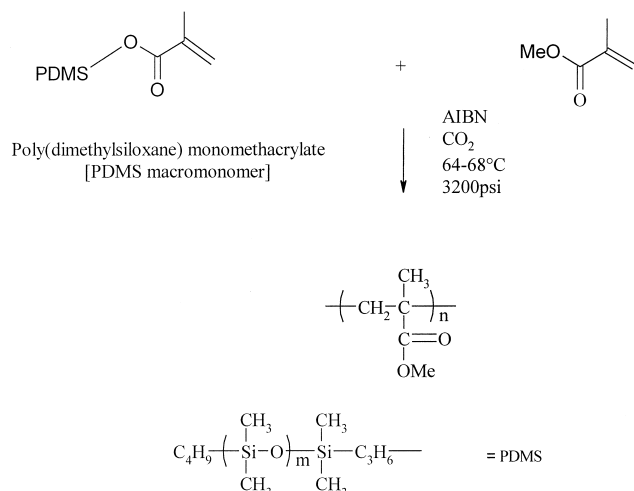


Fig. 1. Reaction scheme for the dispersion polymerisation of methyl methacrylate.

2. Experimental

The PDMS macromonomer ($M_n \sim 10\,000$), and initiator (2,2'-azobis(isobutyronitrile) (AIBN)) supplied by Aldrich, and methyl methacrylate (ICI, inhibited with 2 ppm of Topanol A (a mix of hindered amines)) were used as received. Polymerisations were performed in a 60 ml stainless steel autoclave fitted with a magnetically coupled overhead stirrer with a simple "paddle" blade (NWA GmbH) and motorised driver (RW20, Janke and Kunkel) at 300–400 rpm. High purity carbon dioxide (BOC Gases, SFC Grade) was passed through a drying column prior to use. Molecular weight data were obtained by gel permeation chromatography with chloroform as the solvent (Aldrich) at 30°C using Polymer Laboratories Plgel 5 μm Mixed-D columns and refractive index detector. Calibration was accomplished with PMMA narrow standards (Polymer Laboratories). Both the sample analysis and the calibration were conducted at a flow rate of 1 ml min⁻¹. Scanning Electron Microscopy (SEM) data were collected using a JEOL 6400 SEM. Samples were mounted on an aluminium stub

using an adhesive carbon tab and were gold-coated. ¹H NMR data were collected using a Bruker 300 MHz spectrometer.

3. Results and discussion

Initial experiments on the dispersion polymerisation of methyl methacrylate in scCO₂ were conducted with 10 wt.% macromonomer and 1 wt.% AIBN with respect to MMA monomer (see entry 1 in Table 1). The yield (31%) and molecular weight of the resulting polymer were found to be very low. Exhaustive repetition, and careful checking for contamination, failed to correct this apparent anomaly. Surprisingly, when the reaction was repeated under exactly the same conditions but *in the absence of any stirring*, a high molecular weight polymer was produced in high yield (84%) and with a particulate morphology (see entry 2, Table 1). Multiple repetition of this experiment confirmed the observation. Thus, it appears that efficient stirring of the reaction in scCO₂ enhances or introduces a termination mechanism, which prevents effective polymerisation. These observations contradict those of others [3,10] who have successfully carried out the free radical polymerisation of methyl methacrylate in scCO₂ whilst stirring. Clearly, stirring is desirable to ensure formation of a uniform dispersion and narrower particle size distribution of the polymer product. Moreover on a commercial scale, stirring is essential to ensure thermal homogeneity and to avoid catastrophic thermal runaway.

The interaction between metals and radicals is well known [16], and so could result in termination of the growing radical chain and reduce the chain length of the polymeric material. Some form of radical termination was therefore suggested as a cause for observed differences between the stirred and non-stirred reactions (entries 1 and 2, Table 1). The key question is how? One possible explanation is that in the absence of stirring, a film of PMMA is formed on the internal metal surface of the autoclave in the initial stages of reaction. Such a film would

Table 1
Dispersion polymerisations of MMA in supercritical CO₂

	AIBN (wt.%) ^a	PDMS (wt.%) ^a	Pressure (psi)	Temperature (°C)	Yield	Stirring	M_n^b	PDI ^b	Product ^c
1 ^d	1	10	2500	68.5	31	Yes	36 400	3.8	Oil/tacky solid ^e
2 ^d	1	10	2650	67.5	84	No	106 500	1.8	White powder
3 ^f	0.33	5	4200	65.4	96	Yes	227 800	1.7	White powder
4 ^f	1	5	3300	68.0	92	Yes	90 500	1.9	White powder
5 ^f	1	5	3250	68.0	33	Yes	23 090	2.4	Sticky solid ^e
6 ^f	1	5	3300	64.3	88	Yes	102 300	2.8	White powder

^a The wt.% AIBN and PDMS based on the mass of monomer in the reaction.

^b Determined directly from the reaction product.

^c Appearance of material collected directly from autoclave.

^d Reactions were conducted for 4 h on a 5 g monomer scale.

^e Remaining monomer removed under reduced pressure.

^f Reactions were conducted for 4 h on a 10 g monomer scale.

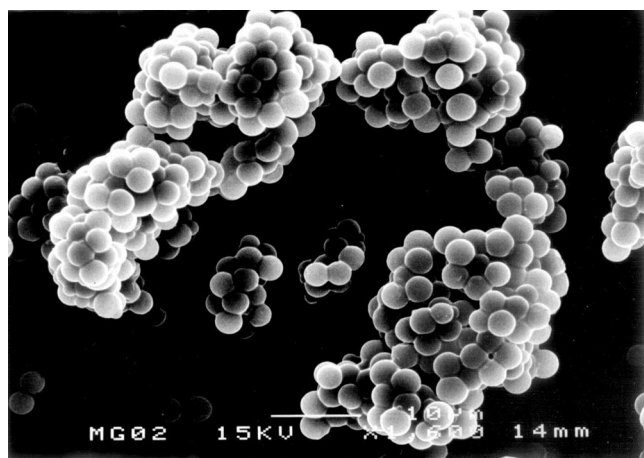


Fig. 2. SEM picture showing particles produced on polymerisation of MMA stabilised with 5% PDMS macromonomer in a PMMA coated cell (conditions as in entry 4, Table 1).

inhibit contact of growing radical terminated chains with the metal wall, limiting radical termination and leading to high yields and molecular weights. However on stirring, this film formation is prevented or the film must be stripped away and re-dispersed by efficient agitation of the MMA/CO₂ reaction medium. Thus, the metal surface is again exposed, leading to radical termination.

Earlier work using the same PDMS macromonomer had not indicated any such difficulty [13]. The main experimental difference was the use of lower initiator concentrations in the previous work (0.33% compared to 1%). Polymerisation was therefore carried out using the lower initiator concentration, mimicking the conditions previously published [13]. This stirred reaction produced poly(methyl methacrylate) as a fine white powder in high yield (entry 3, Table 1). As expected, the lower initiator concentration lead to an increase in molecular weight of the PMMA product ($M_n = 227\,800$). One would also expect an increased molecular weight for a PMMA film formed on the autoclave wall. If sufficiently high, the PMMA film should not re-disperse in the MMA/CO₂ reaction medium. Clearly if this were the case, such a coating should remain intact in the autoclave or dissolve at a much slower rate and would continue to act as a barrier to radical termination for subsequent reactions.

To test this hypothesis, a reaction was subsequently performed in the same autoclave under the original conditions at 1 wt.% AIBN and with stirring. On this occasion, PMMA particles were produced in high yield and with acceptable molecular weight (entry 4, Table 1), indicating that radical termination by the cell wall has been minimised by the PMMA coating. Subsequent repetition of this reaction over 10 occasions showed negligible deterioration in MW and yield. The SEM of this material in Fig. 2(a) shows the formation of particles with average diameter of 2.3 μm .

If our hypothesis is correct, then removal of the PMMA coating should again result in a return to low yields and

molecular weights when stirring. To test this, the internal walls of the autoclave were washed with conc. nitric acid and the surface then lightly abraded with Carbide paper, taking care to leave no metal particles in the cell. Subsequent polymerisation at 1 wt.% AIBN with stirring did indeed result in a largely monomer containing oil, with low molecular weight PMMA (entry 5, Table 1).

The whole procedure was repeated successfully by re-coating the autoclave walls at a low (0.33 wt.%) AIBN concentration, and then subsequently confirming that polymerisation reactions could be performed in the presence of stirring at 1% AIBN. Thus, these results strongly indicate that some form of high molecular weight PMMA coating inhibits radical termination at the exposed metal wall.

However, definitive proof of such a coating requires a sample for analysis. Thus, experiments were targeted at extraction and analysis of PMMA from the autoclave wall. In each case, the autoclave was coated as described previously, and polymerisation of MMA at 1 wt.% AIBN, with stirring, was first performed to confirm the presence of the coating (see for example entry 6, Table 1). In the first extraction experiment, the coated autoclave was loaded with methyl methacrylate and charged with CO₂ at 3200 psi at 67.1°C (see entry 1, Table 2 for conditions) and stirred for 4 h in the absence of AIBN initiator. After venting the scCO₂, analysis of the residue revealed only the MMA monomer. Repetition of the procedure using an MMA/PDMS macromonomer mixture similarly showed only the presence of residual MMA and PDMS macromonomer (entry 2, Table 2) following GPC analysis. Thus, neither MMA/scCO₂ nor MMA/PDMS macromonomer/scCO₂ were sufficiently good solvents for the PMMA.

The extraction process was then repeated in the presence of a commercially available fluorinated co-solvent (Krytox 157FSL) that is soluble in scCO₂ (entry 3, Table 2). On this occasion, the extraction afforded a small amount of white polymeric solid (<300 mg) after removal of monomer and co-solvent under reduced pressure. ¹H NMR spectroscopy showed the solid material to be PMMA with less than 1 wt.% PDMS macromonomer incorporated. The material was predominately syndiotactic, the same tacticity as the bulk material, indicating a similar polymerisation mechanism. A GPC trace of the material (Fig. 3) indicates that this PMMA has a very high molecular weight. The trace also shows a negative peak attributable to residual PDMS macromonomer, which must have been trapped in the PMMA during the original coating procedure.

The PMMA dissolved from the cell wall has a molecular weight considerably higher than the bulk PMMA synthesised in scCO₂. This indicates that a separate process must be occurring at the metal autoclave wall. The molecular weight of this material is in the range normally attributed to PMMA prepared commercially by the cell cast methodology. Typically, the level of initiator used to produce such a high molecular weight (0.01 wt.%) is orders of magnitude lower than in our experiments [17]. This would appear to

Table 2
Washing reactions to remove material from cell wall

	MMA (g)	Surfactant	% Stabiliser	Pressure (psi)	Temperature (°C)	Period of washing	M_n of material recovered	M_w of material recovered	PDI of material recovered
1	10.30	None	–	3200	67.1	4 h	NA ^a	NA ^a	NA ^a
2	10.17	PDMS	5	3100	66.1	15 h	10 400 ^b	11 900 ^b	1.14 ^b
3	10.01	Fluorinated co-solvent	1	3200	64.8	16 h	848 200 ^b	2 213 400 ^b	2.61 ^b

^a Little or no material obtained.

^b Determined using gel permeation chromatography relative to poly(styrene) standards (M_w 580–7 500 000) using chloroform as the solvent.

suggest that the wall coating is laid down in the early stages of the reaction. During this period, the metal wall destroys (by some form of quench or chain transfer) many of the initiating radicals and short chain propagating radicals. This leads to a low concentration of active radical centres and a high concentration of MMA at or near the wall. Under these conditions, a high molecular weight PMMA coating is formed. This is the case for the lower initiator concentration (0.33 wt.%), but at higher concentrations (1 wt.% AIBN), the higher radical flux essentially overrides the quenching by the wall and any PMMA coating formed at the wall must be of a lower molecular weight, and is redispersed or dissolved in the reaction mixture.

In order to investigate further the effect of metals, a number of steel test strips (surface area $\sim 2 \text{ cm}^2$) were placed in the centre of the autoclave during a stirred polymerisation under different initiator concentrations (Table 3). The PMMA produced on the surface of the metal strips has higher M_n and M_w than that of the bulk material (entries **1** and **2**, Table 3), confirming that the same process must be occurring. SEM images of the material produced using 1% AIBN show a thin film of polymer on the metal surface formed from smaller particles (Fig. 4). By contrast, no such higher molecular weight coating could be detected on glass strips (entry **3**, Table 3) indicating that a metal/radical interaction must be present to produce the high molecular weight coated PMMA.

Interestingly, the PMMA coating on the metal strips appears to have a similar molecular weight regardless of the amount of initiator employed. Moreover, this molecular weight is considerably lower than that of the PMMA isolated from the wall of the autoclave (Table 2). This observation may well be a function of the type of material. The autoclave body is constructed from a high strength, high nickel content stainless steel (Grade 4980: 0.03% C, 1.03% Mn, 15% Cr, 1.15% Mo, 25% Ni). Such materials are widely used for high pressure applications. The head unit is 316 stainless steel (0.08% C, 2% Mn, 16% Cr, 2% Mo and 10% Ni) whereas the strips are of conventional steel (0.12% C, 0.60% Mn, 0.05% S and 0.05% P, with negligible Ni, Cr content).

Table 3
Dispersion polymerisations of MMA in supercritical CO₂ stabilised with PDMS macromonomer containing metal or glass test strips

	% AIBN ^a	Yield (%)		M_n	M_w	PDI
1 ^b	0.33	80	Bulk material	169 200	348 200	2.05
			Metal strip	240 700	457 500	1.91
2 ^b	1	89	Bulk material	119 800	271 200	2.26
			Metal strip	293 400	488 100	1.66
3 ^b	1	91	Bulk material	140 600	294 200	2.09
			Glass strip	146 600	313 700	2.13

^a wt.% relative to monomer.

^b Reactions carried out on a 10 g scale in CO₂ at 3250 psi at 65.6°C using 5% PDMS macromonomer.

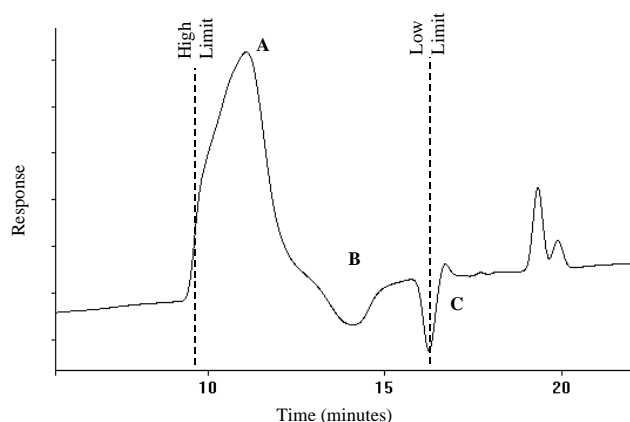


Fig. 3. GPC trace showing high molecular weight PMMA from cell wall (peak A), residual PDMS macromonomer (negative peak B) and MMA (negative peak C) obtained from washing of the autoclave using a scCO_2 /fluorinated co-solvent/MMA mixture.

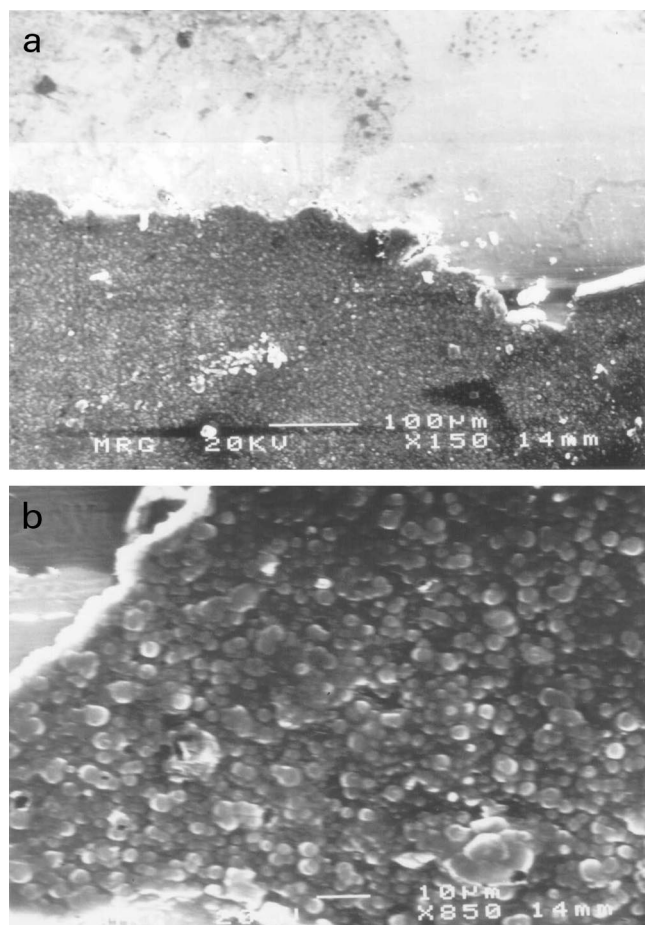


Fig. 4. SEM pictures showing the material produced on the surface of a metal test strip on the polymerisation of MMA using 5% PDMS macromonomer and 1% AIBN (see Table 3 for exact reaction conditions).

4. Conclusions

The free radical polymerisation of methyl methacrylate in scCO_2 is very sensitive to the condition of the internal surface of the high pressure autoclave. When the polymerisation is efficiently agitated, PMMA is produced only in low yield, with low molecular weight and poor morphology. The exposed metal surface appears to terminate the growing polymer and inhibit polymer formation. This effect may well be exacerbated in our reactions by the high rate of diffusion in scCO_2 , increasing the rate of collisions between the radicals and the wall.

Our experiments have shown that by careful control of initiator concentration, a durable high molecular weight coating can be deposited on the walls of the autoclave. This coating appears to prevent radical/metal termination and the exact mechanism for the formation of this high molecular weight PMMA is still under investigation.

High pressure autoclaves are normally constructed of high strength alloys of similar composition to that of our own autoclave. Thus, this paper highlights the need to consider carefully the choice of materials, and methods for preventing deleterious interaction with the reaction mixture. To the best of our knowledge such effects have not been reported before, but little published data has been presented which describes efficient stirring and the materials of autoclave construction. We believe that the data presented here will have considerable impact upon the development of commercial scale supercritical fluid processes.

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