

Macromonomer surfactants for the polymerisation of methyl methacrylate in supercritical CO₂

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Abstract

Free radical polymerisation of methyl methacrylate in supercritical CO₂ requires addition of a surfactant (amphiphatic macromolecule) to produce poly(methyl methacrylate) (PMMA) in high yield and molar mass and with well-defined particle sizes. This paper describes the use of poly(dimethylsiloxane)monomethacrylate macromonomers in stabilising the free radical polymerisation of methyl methacrylate in supercritical CO₂. In particular, the effects of surfactant molar mass (2–10 kD) and concentration on the nature of the product PMMA are examined. It is found that the 2 kD surfactant is the most effective at low (wt./wt.) concentrations and may be a more viable option for industrial production than the higher molar mass surfactants, although the particle sizes of the PMMA products are different. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Increasing concern about the effects of the release of volatile organic compounds (VOCs), chlorofluorocarbons (CFCs) and aqueous waste into the environment has prompted work in recent years on development of replacement solvents, with supercritical fluids attracting much of the attention.² Most studies have focused on the use of supercritical carbon dioxide, which offers a solvent choice that

- is environmentally sound (zero net VOC emissions);
- is accessible and inexpensive;
- is non-toxic and non-flammable;
- can be recycled; and
- has an easily attainable critical point ($T_c = 31.1^\circ\text{C}$, $P_c = 73.8$ bar).

Supercritical carbon dioxide (scCO₂) has generated much interest in the polymer industry as a potential solvent for polymerisation reactions [1–4]. There is no chain transfer to

CO₂ in free radical polymerisations and supercritical fluids, in general, allow the easy separation of the polymer product from the reaction medium, producing the polymer in powder form by simply venting the reaction mixture. The solvent power of a supercritical fluid is dependent on its density and hence on the pressure of the fluid. For polymers, the dissolving power of supercritical CO₂ is similar to that of fluorocarbons. CO₂ is essentially a non-solvent for most polymers, including lipophilic and hydrophilic polymers, but tends to be a reasonable solvent for many amorphous fluoropolymers and siloxanes [5,6]. Because of these solvent characteristics, in most cases it is difficult to produce good yields of high molar mass polymers through solution polymerisation in scCO₂, since the polymer product inevitably precipitates from the reaction medium. Much work has therefore focused on the use of surfactants (amphiphatic macromolecules) to stabilise a dispersion of the growing polymer product in scCO₂. These surfactants consist of a ‘CO₂-philic’ section, almost without exception a siloxane or fluorocarbon, and a ‘CO₂-phobic’ section to interact with the polymer being synthesised. The three main approaches to developing effective surfactants for use in scCO₂ have been:

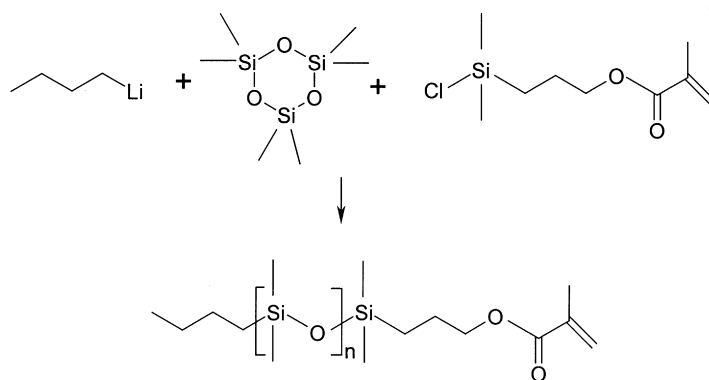
1. Use of CO₂-compatible polymers as surfactants, e.g. poly(1,1-dihydroperfluorooctyl acrylate) poly(FOA) [7].
2. Use of ‘CO₂-philic’ surfactants with a suitable

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² Chem. Rev. provides an excellent overview of the state of the art in the field. Chem Rev 1999;99(2):353–634.



Scheme 1.

polymerisable group to be incorporated into the growing polymer chain forming an in situ graft copolymer [8–10].

- Use of *block* copolymers with ‘CO₂-philic’ and ‘CO₂-phobic’ *blocks* [11–13] and *graft* systems with a ‘CO₂-phobic’ backbone and ‘CO₂-philic’ *graft* chains [14,15].

The first reported heterogeneous polymerisation of vinyl monomers in liquid and supercritical CO₂ is contained in a patent filed by the Sumitomo Chemical Company in 1968, in which they took a series of vinyl monomers, including methyl methacrylate, and produced polymers and copolymers by precipitation polymerisation [16]. In 1992, the group of DeSimone at North Carolina reported the free radical initiated homogeneous polymerisation of 1,1-dihydroperfluorooctyl acrylate (FOA) in scCO₂ [17], triggering the surge of interest in polymerisation in scCO₂ which continues to this day. In 1994, further work by DeSimone et al. demonstrated the dispersion polymerisation of methyl methacrylate in supercritical CO₂ using poly(1,1-dihydroperfluorooctyl acrylate) (polyFOA) as the surfactant [7]. The resulting poly(methyl methacrylate) was of high molar mass and in the form of evenly sized spherical particles. Many fluorinated surfactants can be expensive and this has stimulated work on potentially cheaper siloxane-based alternatives. A macromonomer approach using poly(dimethylsiloxane)monomethacrylate as a reactive surfactant resulted in formation of poly(methyl methacrylate) containing a small amount of incorporated poly(dimethylsiloxane) macromonomer [8].

At the outset of the work described here, no report of the use of siloxane-based surfactants had yet been published and the aim was to undertake a systematic study of the effects of a series of siloxane macromonomers of different molar masses on the polymerisation of methyl methacrylate in supercritical CO₂. One result of this study was the discovery of the ‘wall effect’ in radical polymerisations in scCO₂, the important consequences of which have been the subject of a separate publication [18].

2. Experimental

2.1. Materials

All reactants were used as received unless stated otherwise. Hexamethylcyclotrisiloxane (D₃) (Aldrich Chemical Company) was distilled from calcium hydride prior to use. 3-(Methacryloxy)propyldimethylchlorosilane (Monomer Polymer & Dajac) was distilled in vacuo prior to use. Tetrahydrofuran (THF) was dried over calcium hydride and distilled prior to use. 100–120° Petroleum ether was distilled prior to use. Methyl methacrylate (Aldrich) was distilled in vacuo prior to use. 2,2′-Azobis(2-methylpropionitrile), AIBN, (Aldrich) was recrystallised from ethanol. Poly(dimethylsiloxane)monomethacrylate of nominal molar mass 10 kD was obtained from Aldrich. *n*-Butyllithium was 1.6 molar in hexane (Aldrich).

2.2. Instrumentation

Gel permeation chromatography (GPC) was carried out using a Waters 510 HPLC pump, THF as eluent pumped at 1.0 cm³ min⁻¹ through a Polymer Laboratories guard column, a Polymer Laboratories PLGel 5 μm 8 × 600 mm² column. A BRMA ERC-7510 RI detector is used to monitor the column output and the data are manipulated using Millipore Millennium software. Polystyrene standards were used for calculating molar mass data.

¹H nuclear magnetic resonance (NMR) spectroscopy was undertaken on a Bruker AC 300 spectrometer operating at 300.15 MHz.

Scanning electron microscopy was carried out on a JEOL 6400 or a Hitachi S3200 Scanning Electron Microscope. Samples were mounted on an aluminium stub using an adhesive carbon tab and were gold coated.

2.3. Synthesis of poly(dimethylsiloxane)monomethacrylate (Scheme 1) [19,20]

Hexamethylcyclotrisiloxane (D₃) (5.06 g) was dissolved in cyclohexane (14 cm³) in a dry round-bottom flask to give

Table 1
Synthesis and molar mass data for macromonomers

Nominal molar mass	10 000	5000	2000
Butyl lithium (mmol)	Aldrich	1.005	2.51
Volume (cm ³)		0.63	1.57
Terminator (mmol)	–	2.01	5.03
Volume (cm ³)		0.45	1.13
Product M_n from NMR	10 200	5000	1800
Product M_n from GPC	10 900	4500	1700
Product PDI from GPC	1.08	1.12	1.15

a 36% weight/volume solution. The required amount of *n*-butyllithium was added to initiate polymerisation, and the mixture stirred for 2 h at room temperature. THF (1.5 cm³, 10 vol%) was added by syringe and the reaction stirred under nitrogen for 48 h. The required quantity of 3-(methacryloxy)propyldimethylchlorosilane (2 mol eq.) was added to terminate the reaction. Lithium chloride precipitated and was removed by filtration. The solvent was removed and the polymer washed with methanol and dried under vacuum (yield up to 95%). ¹H NMR spectroscopy was used to confirm the structure of the products. For the 5 kD product, δ : (ppm in CDCl₃) 6.10 (s, 1H) and 5.54 (s, 1H) [=CH₂], 4.10 (t, 2H) [Si–CH₂–CH₂–CH₂–O], 1.94 (s, 3H) [–C(=CH₂)–CH₃], 1.70 (m, 2H) [Si–CH₂–CH₂–CH₂–O], 1.25 (m, 6H) [CH₃–(CH₂)₃–Si], 0.88 (t, 2H) [Si–CH₂–CH₂–CH₂–O], 0.57 (m, 3H) [CH₃–CH₂], 0.13 (s) [O–Si(CH₃)₂–CH₂] and 0.07 (s, 380H) [O–Si(CH₃)₂–O]. The molar mass of the resulting polymer was determined using GPC (Table 1). Elemental analysis gave: found C 34.1%, H 8.4%; calculated C 34.0%, H 8.2%. The corresponding 2 kD macromonomer gave the following analysis: found C 36.8%, H 8.6%; calculated C 36.2%, H 8.4%.

2.4. Non-aqueous dispersion polymerisation of methyl methacrylate

MMA, poly(dimethylsiloxane)monomethacrylate and

Table 2
Results of polymerisation of methyl methacrylate in 100–120° petroleum ether

Composition (wt.%)		Yield (%)	GPC	
MMA	Surfactant		M_n ($\times 10^3$)	PDI
100.0	0.0	68	89	4.3
89.9	10.1 ^a	92	75	3.0
90.0	10 ^a	87	63	2.4
95.0	5.0 ^a	81	103	3.7
97.4	2.6 ^a	77	109	4.1
89.9	10.1 ^b	89	128	3.3
95.0	5.0 ^b	87	119	3.8
97.5	2.5 ^b	72	63	6.0
97.5	2.5 ^b	76	106	4.9

^a Poly(dimethylsiloxane)monomethacrylate (Aldrich).

^b Poly(dimethylsiloxane)monomethacrylate (nominal molar mass = 5000).

AIBN (0.1 wt.%) were added to the polymerisation vessel under nitrogen in the ratios shown in Table 2. 100–120° petroleum ether (16 g) was added and the reaction heated with stirring at 70°C for 72 h. The product, in the form of a white powder, was collected by filtration.

2.5. Polymerisation of methyl methacrylate in scCO₂

The reaction vessel (NWA) was charged with methyl methacrylate (10g), 2,2'-azobis(2-methylpropionitrile) (1 wt.% wrt monomer) and the required amount of surfactant, closed and filled with CO₂. The temperature was raised to 65°C and the pressure to the required level and the system left to stand, without stirring, for 4 h. After 4 h the temperature was allowed to fall to room temperature and then the vessel was vented. The resulting poly(methyl methacrylate) was collected, washed with hexane, and analysed by GPC and ¹H NMR spectroscopy (Tables 3–5). A series of experiments was also carried out with the 10 kD macromonomer at 5 wt.% wrt monomer addition level, varying the pressure from 2700 to 4100 psi and measuring the amount of surfactant in the PMMA product.

3. Results and discussion

Poly(dimethylsiloxane)monomethacrylate of molar mass 10 kD is commercially available (Aldrich) while those of nominal molar mass 5 and 2 kD were synthesised by anionic ring opening polymerisation of D₃ using *n*-butyllithium, followed by termination with 3-(methacryloxy)propyldimethylchlorosilane (Scheme 1) [19–21]. All surfactants were analysed by NMR spectroscopy which confirmed the synthesis of the expected structures. A typical ¹H NMR spectrum of the 2 kD molar mass PDMS monomethacrylate is shown in Fig. 1. Resonances for the PDMS methyl groups dominate the spectrum at 0.07 ppm, while the methacrylate methyl protons are visible at 1.94 ppm. Vinyl proton resonances are seen clearly at ca. 5.5 and 6.1 ppm. It was possible to obtain an approximate value for the number average molar mass of the macromonomers from the ratio of PDMS signals to vinyl proton signals, although the large difference in the integrals of these signals probably introduces significant errors. Molar mass data calculated from the NMR spectra are shown in Table 1, along with those obtained from GPC. The measured molar masses are close to the target values and there is surprisingly good agreement between the NMR and GPC data, considering that the latter were measured versus polystyrene standards. The molar mass distributions of the macromonomers are narrow, typically in the range 1.1–1.2, as expected for a well-controlled anionic polymerisation.

The surfactants were evaluated for their effectiveness as stabilisers for the polymerisation of methyl methacrylate in scCO₂ using AIBN as the initiator. Although these surfactants are not optimised for non-aqueous dispersion polymerisation in hydrocarbon solvents, it was nonetheless of interest

Table 3

Poly(dimethylsiloxane)monomethacrylate, $M_n = 10\,000$, as surfactant for the polymerisation of MMA in supercritical CO_2

AIBN% (wt.)	PDMS ^a % (wt.)	Temperature (°C) (average)	Pressure (psi) (average)	Yield (%)	$M_n (\times 10^3)$ (GPC)	PDI (GPC)	PDMS ^a in polymer (wt.%)	
							Before wash	After wash
1	0	67.1	2426	15	15	4.2	–	–
1	0.2	68.8	2341	61	36	2.3	0.20	0.08
1	1	68.8	2508	71	89	2.2	1.96	0.40
1	2	69.8	2530	66	85	2.2	1.96	0.70
1	5	68.1	2514	78	97	2.1	2.91	0.79
1	10	67.3	2651	84	106	1.8	9.10	2.91

^a Poly(dimethylsiloxane)monomethacrylate.

to compare their efficiency in scCO_2 with their performance in petroleum ether and this was carried out for two of the monomethacrylates. The solvent power of scCO_2 has sometimes (erroneously) been compared to that of hexane. The main aim of the study was to compare the effectiveness of different molar mass surfactants of the macromonomer type. Although the 10 kD macromonomer has been reported to be an effective stabiliser at 3.5 wt.% concentration, lower molar mass surfactants were not studied [8]. A recent report [22] compares the effectiveness in acrylic copolymerisation of the 10 kD methacrylate macromonomer with two lower molar mass macromonomers with vinyl termination; however, no firm conclusions can be drawn from this report since different polymerisable groups were used and a systematic study of surfactant addition level was not reported. The effect of macromonomer molar mass is important since; (a) it is known that molar mass influences dispersion efficiency in conventional non-aqueous dispersion polymerisation using such surfactants [23]; (b) the ability to use shorter chain PDMS systems at an equivalent molar concentration could have important implications for the cost of supercritical polymerisation on an industrial scale; and (c) the different PDMS chain length could affect the ability to extract any residual surfactant from the polymer product and/or change the effect of any incorporated surfactant on the properties of the polymer.

The polymerisation reactions of MMA using 100–120° petroleum ether as a solvent, where the PMMA is produced

under non-aqueous dispersion polymerisation conditions, show a rough trend where the product has a higher molar mass when more macromonomer is present, although the trend is not general. The PDIs of these reaction products are high, indicating a broad molar mass distribution. The PMMA formed in these reactions has a stereochemistry that is mostly syndiotactic (57–60%) and atactic (33–36%) with very little isotactic product formed, as would be expected for a typical free radical polymerisation [24,25]. SEM images (not shown) show the polymer products to have a cauliflower-like structure, consisting of small, approximately 2 μm diameter particles which appear to be stuck together. The particles are not perfectly spherical, suggesting that although the macromonomer is acting as a stabiliser of the dispersion, it is not optimised for this system. This is not entirely surprising since the siloxane was not designed for use in petroleum ether as solvent.

Tables 3–5 show the results for the polymerisations of methyl methacrylate in supercritical CO_2 using macromonomer surfactants of molar mass 10, 5 and 2 kD, respectively. All of these polymerisation reactions were undertaken in the absence of vigorous stirring since previous work had shown that such stirring promotes an inhibitory effect of the metal wall of the vessel on the free radical polymerisation process, resulting in formation of oligomeric products [18]. In terms of yield and molar mass of the product poly(methyl methacrylate) (PMMA), it can be seen that at least 2 wt.% of the 10 000 molar

Table 4

Poly(dimethylsiloxane)monomethacrylate, $M_n = 5000$, as surfactant for the polymerisation of MMA in supercritical CO_2

AIBN% (wt.)	PDMS ^a % (wt.)	Temperature (°C) (average)	Pressure (psi) (average)	Yield (%)	$M_n (\times 10^3)$ (GPC)	PDI (GPC)	PDMS ^a in polymer (wt.%)	
							Before wash	After wash
1	0	69.1	2566	22	12	3.9	–	–
1	0.2	70.1	2660	63	25	4.4	0.99	0.30
1	1	69.8	2790	88	84	2.1	1.96	0.99
1	2	68.9	2806	86	91	2.3	2.44	1.48
1	5	69.6	3060	90	113	1.9	5.22	2.44
1	10	68.7	2876	92	89	2.5	11.14	3.38
1	20	69.2	2800	97	113	2.1	20.08	1.96

^a Poly(dimethylsiloxane)monomethacrylate.

Table 5
Poly(dimethylsiloxane)monomethacrylate, $M_n = 2000$, as surfactant for the polymerisation of MMA in supercritical CO_2

AIBN % (wt.)	PDMS ^a % (wt.)	Temperature (°C) (average)	Pressure (psi) (average)	Yield (%)	$M_n (\times 10^3)$ (GPC)	PDI (GPC)	PDMS ^a in polymer (wt.%)	
							Before wash	After wash
1	0	66.0	2900	52	44	3.7	–	–
1	0.2	65.0	3200	93	105	2.6	0.04	0.04
1	1	66.0	3150	97	102	2.5	0.38	0.19
1	2	66.0	3100	94	110	2.2	1.98	0.38
1	5	66.0	3250	97	95	2.1	4.37	0.92
1	10	66.5	3200	96	162	2.0	7.42	1.31

^a Poly(dimethylsiloxane)monomethacrylate.

mass poly(dimethylsiloxane)monomethacrylate surfactant is required to stabilise the dispersion during polymerisation. These reactions result in good yields of PMMA with a high molar mass and moderate polydispersity (PDI). The SEM micrographs show that spherical particles with a diameter of 2–3 μm are produced at concentrations of 5% and above (Fig. 2), correlating well with previously published data [8]. Similarly, for the 5000 molar mass poly(dimethylsiloxane)monomethacrylate at least 5 wt.% of the surfactant is required for the production of good quality poly(methyl methacrylate) with well defined spherical morphology. Surprisingly, for the 2000 molar mass poly(dimethylsiloxane)monomethacrylate only 0.2 wt.% of surfactant is required to produce good quality polymer in terms of molar mass and PDI; however, the SEM micrographs show that 2% is the minimum surfactant concentration required to produce well defined spherical particles (Fig. 3). It is interesting to note that the particles formed in the presence of the 2 kD surfactant are approximately twice the diameter of those formed using the 10 kD surfactant, at all the surfactant concentrations studied. This can be compared with a study of preformed graft copolymer surfactants by Lepilleur and Beckman [14], who found that a large number of shorter grafts produced PMMA particles of smaller diameter than a small number of longer grafts. Since the precise structures of the in situ graft copolymer surfactants formed in our case are not known, it cannot be stated with certainty that these results are contradictory. It is also

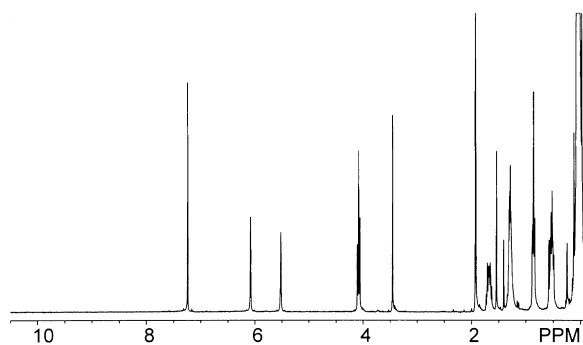


Fig. 1. ^1H NMR spectrum of poly(dimethylsiloxane)monomethacrylate, $M_n = 2000$.

possible that the greater particle size is indicative of a greater amount of agglomeration occurring during polymerisation, although the particle size distribution is reasonably monodisperse.

In all cases, ^1H NMR spectroscopy is used to calculate the incorporation of the surfactant into the polymer chain, and it can be seen that once the polymer has been washed with hexane there is little incorporation of the surfactant (Tables 3–5). This is illustrated graphically in Fig. 4 for the 5 kD macromonomer before and after a 24 h wash with pentane. It is interesting to note, however, that the 5 kD surfactant shows the greatest incorporation into the PMMA product, both before and after washing. The 2 kD surfactant shows slightly less incorporation than the 10 kD surfactant. Whether or not these results are indicative of different degrees of copolymerisation with the MMA would require more work to ascertain since at these low levels, NMR spectroscopy cannot provide sufficiently accurate data. Steric factors alone might suggest that copolymerisation would be more efficient for lower molar mass macromonomers, but the results do not totally support this hypothesis; however, in such complex heterogeneous systems, other factors may play an important role [26,27]. Differences in the degree of association of macromonomer surfactants of different chain length may be important in

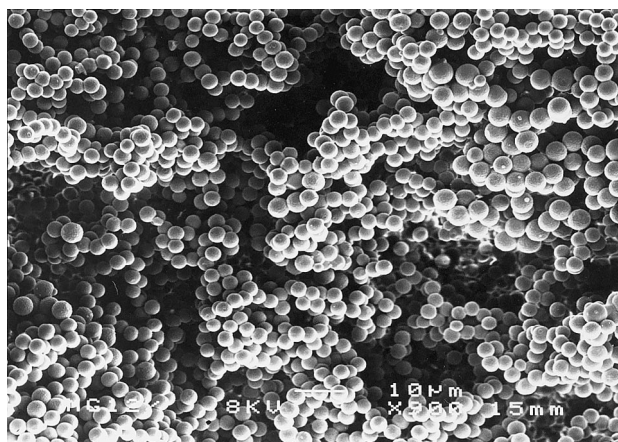


Fig. 2. SEM micrograph of PMMA formed using 5% poly(dimethylsiloxane)monomethacrylate, $M_n = 10000$, as surfactant.

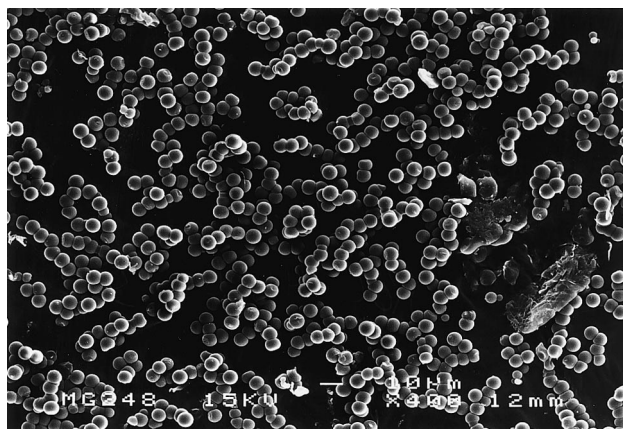


Fig. 3. SEM micrograph of PMMA formed using 2% poly(dimethylsiloxane)monomethacrylate, $M_n = 2000$, as surfactant.

determining copolymerisation rate, while termination processes may also be affected. The effect of polymerisation pressure on surfactant incorporation was also studied and the results are summarised in Fig. 5. It can be seen that the degree of incorporation (copolymerisation?) of the macromonomer increases with pressure up to ca. 3200 psi, above which it is invariant. The compatibility of the PDMS segments with the carbon dioxide will increase with increasing pressure [9,10,28], thus changing the surfactant association processes and perhaps increasing copolymerisation rate. The ^1H NMR spectra show that the samples are ca. 60% syndiotactic, which is similar to the results found for the non-aqueous dispersion polymerisation. Generally, above the surfactant concentration needed to stabilise the dispersion, the molar mass of the resultant PMMA is invariant with concentration. PDI values for the polymers are generally slightly greater than two for surfactant concentrations above the minimum required to stabilise the dispersion and much lower than those found for the products synthesised in petroleum ether, again suggesting that these surfactants work better in scCO_2 than the hydrocarbon solvent. Other possible reasons for this include different degrees of chain transfer to the solvent and/or

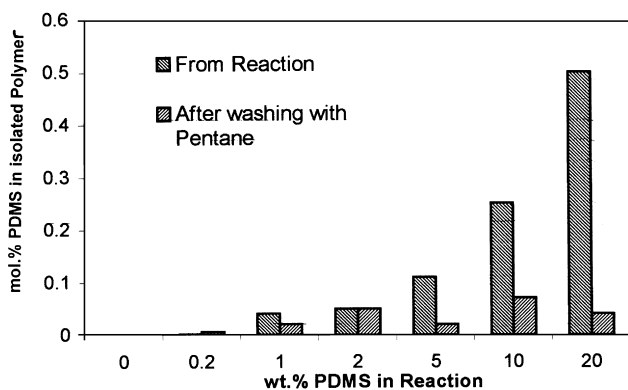


Fig. 4. Concentration of 5 kD macromonomer ('PDMS') in PMMA after polymerisation and following pentane wash.

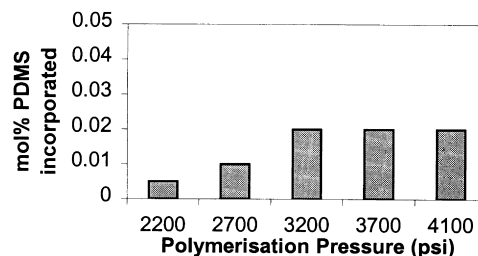


Fig. 5. Concentration of 10 kD macromonomer ('PDMS') in PMMA after polymerisation at different pressures.

differences in MMA partitioning between the continuous phase and the monomer-swollen particles.

The 2 kD molar mass surfactant thus provides more effective stabilisation on a wt./wt. basis than the 10 kD surfactant. Converting the concentration to a molar basis, however, results in a different conclusion. The 2 kD and 10 kD surfactants are effective at molar concentrations of 10^{-3} and 5×10^{-4} mol.%, respectively. Thus, at a molecular level, the 10 kD surfactant is the more effective, each macromonomer molecule being able to stabilise the polymerisation of 2000 monomer molecules, compared to only 1000 per 2 kD molecule. This molar view may also go some way to explaining our observations on the incorporation of the PDMS macromonomer into the growing PMMA chains. It is well established that there is an optimum balance between the size of the anchoring group (chain length of actual surfactant molecule) and the amount of scCO_2 -soluble (PDMS) component if adequate stabilisation is to be achieved [4,9,14,15]. From a cost and industrial manufacturing point of view, the wt./wt. effects may be the most significant. Assuming 100% yield of the macromonomer based on starting D_3 cyclotrisiloxane (or at least equivalent yields of the different molar mass surfactants), it is possible to calculate the amount of D_3 required to synthesise sufficient surfactant to polymerise, say, 1 metric tonne of MMA. This works out at 48.8 kg of D_3 for the 10 kD surfactant and 17.6 kg for the 2 kD surfactant. Assuming that the manufacturing costs are similar for each surfactant and that differences in costs of the other (more minor) chemical components are insignificant (an assumption which is greatest for the 3-(methacryloxy)propyldimethylchlorosilane), it can be seen that the 2 kD surfactant makes more effective use of the expensive siloxane component and may be a more cost effective approach on an industrial scale. This conclusion also assumes that the difference in particle size is not a crucial factor in the use of the product.

4. Conclusions

This work has shown that poly(dimethylsiloxane)monomethacrylates with a variety of molar masses are successful surfactants for the polymerisation of methyl methacrylate in

supercritical CO₂, producing particulate polymer above a critical concentration which is dependent on the molar mass of the macromonomer. The poly(dimethylsiloxane)-monomethacrylate with a nominal molar mass of 2000 is a surprisingly good surfactant at low wt./wt. concentrations, which may make it a more viable option for future commercial exploitation than the higher molar mass surfactants.

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References

- [1] Shaffer KS, DeSimone JM. *Trends Polym Sci* 1995;3:146–53.
- [2] Cooper AI, DeSimone JM. *Curr Opin Solid State Mater Sci* 1996;1:761–8.
- [3] Canelas DA, DeSimone JM. *Adv Polym Sci* 1997;133:103–40.
- [4] Kendal JL, Canelas DA, Young JL, DeSimone JM. *Chem Rev* 1999;99:543–63.
- [5] Rindfleisch F, DiNoia TP, McHugh MA. *J Phys Chem* 1996;100:15581–7.
- [6] McHugh M. Proceedings of 'Fluorine in Coatings II', PRA, Munich, 24–26 February 1997.
- [7] DeSimone JM, Maury EE, Menciloglu YZ, McClain JB, Romack TJ, Combes JR. *Science* 1994;265:356–9.
- [8] Shaffer KA, Jones TA, Canelas DA, DeSimone JM, Wilkinson SP. *Macromolecules* 1996;29:2704–6.
- [9] O'Neill ML, Yates MZ, Johnston KP, Smith CD, Wilkinson SP. *Macromolecules* 1998;31:2838–47.
- [10] O'Neill ML, Yates MZ, Johnston KP, Smith CD, Wilkinson SP. *Macromolecules* 1998;31:2848–56.
- [11] Guan Z, DeSimone JM. *Macromolecules* 1994;27:5527–32.
- [12] Canelas DA, DeSimone JM. *Macromolecules* 1997;30:5673–82.
- [13] Hems WP, Yong TM, Van Nunen JLM, Cooper AI, Holmes AB, Griffin DA. *J Mater Chem* 1999;9:1403–7.
- [14] Lepilleur C, Beckman EJ. *Macromolecules* 1997;30:745–56.
- [15] Giles MR, O'Connor, SJ, Hay JN, Winder RJ, Howdle SM. *Macromolecules*, Submitted for publication.
- [16] Sumitomo, French Patent, (1968) 1524533 and US Patent (1970) 3522228.
- [17] DeSimone JM, Guan Z, Elsbernd CS. *Science* 1992;257:945–7.
- [18] Christian P, Giles MR, Howdle SM, Major RC, Hay JN. *Polymer* 2000;41:1251–6.
- [19] Cameron GG, Chisholm MS. *Polymer* 1985;26:437–42.
- [20] Smith SD, DeSimone JM, Huang H, York G, Dwight DW, Wilkes GL, McGrath JE. *Macromolecules* 1992;25:2575–81.
- [21] Ito K. *Prog Polym Sci* 1998;23:581–620.
- [22] Wang D, DeSimone JM. *ACS PMSE Preprints* 1999;80:526–7.
- [23] Walbridge DJ. In: Barrett KEJ, editor. *Dispersion polymerisation in organic media*, London: Wiley, 1975. p. 45–114.
- [24] Bovey FA, Tiers GVD. *J Polym Sci* 1960;44:173–82.
- [25] Bovey FA. *J Polym Sci* 1960;46:59–64.
- [26] Capek I, Akashi M. *JMS-Rev Macromol Chem Phys* 1993; C33(4):369–436.
- [27] Meijs GF, Rizzardo E. *JMS-Rev Macromol Chem Phys* 1990; C30(3–4):305–77.
- [28] Meredith JC, Johnston KP. *Macromolecules* 1998;31:5518–28.