JOURNAL OF Materials CHEMISTRY

Dispersion polymerisation of methyl methacrylate in supercritical carbon dioxide—evaluation of well defined fluorinated AB block copolymers as surfactants

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Received 9th February 1999, Accepted 8th April 1999

Application of the 'screened anionic polymerisation' method to the synthesis of well-defined AB block copolymers derived from methyl methacrylate and fluorinated methacrylate monomers has provided a family of tuneable surfactants for the free radical dispersion polymerisation of methyl methacrylate in supercritical carbon dioxide. Poly(methyl methacrylate) is obtained with excellent conversion and high molecular weight. Block copolymers having higher molecular weight and higher fluorine contents are superior surfactants, and by systematic evaluation of the parameters in the dispersion polymerisation of methyl methacrylate, discrete polymer particles can be obtained.

Introduction

Supercritical carbon dioxide ($scCO_2$) possesses interesting solvent properties which have been applied to a range of separation and extraction processes,[1,2] as well as organic reactions[3] and polymerisations.[4,5] Carbon dioxide is an attractive medium for such processes as it is non-toxic, non-flammable, inexpensive and has a relatively low critical temperature ($T_c = 31.1$ °C) and an accessible critical pressure ($p_c = 72$ bar).

Although CO_2 is a good solvent for many low molecular weight compounds such as monomers, it is a poor solvent for most polymers except certain amorphous fluoropolymers and polysiloxanes. This solubility characteristic enabled DeSimone and coworkers to synthesise a variety of acrylic and styrenic fluoropolymers in $scCO_2$ *via* homogeneous free radical polymerisation methods.[6,7] However, most lipophilic and hydrophilic polymers are insoluble in $scCO_2$ and therefore heterogeneous polymerisation techniques are required.[8]

Dispersion polymerisation constitutes an important heterogeneous technique characterised by an initially homogeneous state where the monomer, initiator and stabiliser are soluble in the continuous phase.[9,10] As the polymerisation progresses the resulting polymer becomes insoluble in the continuous phase, but flocculation is prevented either by steric or electrostatic stabilisation. Steric stabilisation usually involves an amphiphilic graft or block copolymer which is adsorbed as a layer on the surface of the growing polymer particle. This layer is partially solvated by the continuous phase and prevents the polymer particles from coalescing by a steric mechanism. Most steric stabilisers have been based on block or graft copolymers consisting of two components—one soluble and one insoluble in the continuous phase. The insoluble component, or anchor group, associates with the dispersed polymer phase. The anchor group can also be designed to react chemically or to graft onto the dispersed polymer after adsorption. The main criteria for the soluble component of the stabiliser are that it should be freely soluble in the continuous phase and also sufficiently bulky to promote steric stabilisation. An effective stabiliser must have the correct balance of soluble and insoluble components (*i.e.*, a good 'anchor-to-soluble ratio').

Recently, a number of groups have reported the dispersion polymerisation of methyl methacrylate (MMA) and styrene in $scCO_2$ using a variety of dispersants. DeSimone employed fluoroacrylate homopolymers,[11,12] fluoroacrylate-*block*-styrene,[13] and poly(siloxane-*block*-styrene)[14] copolymers for the dispersion polymerisation of MMA and styrene. Beckman[15] synthesised graft copolymers based on a poly(methacrylate-*co*-hydroxyethyl methacrylate) backbone with graft chains of poly(perfluoropropylene oxide). DeSimone[16] has also evaluated a reactive silicone macromonomer for the dispersion polymerisation of MMA in $scCO_2$. A major question in this area concerns the effect of well-defined block copolymers containing poly(methacrylate) and poly(fluoroalkyl methacrylate) segments as potential stabilisers for the dispersion polymerisation of MMA in $scCO_2$.

We report here the design of tailor-made fluorinated AB block copolymers and their use in the dispersion polymerisation of MMA in $scCO_2$. The A block of the copolymer is poly(methyl methacrylate) (PMMA), which is insoluble in $scCO_2$ and has an affinity for the growing polymer. The B block consists of a poly(fluoroalkyl methacrylate) (PFMA) polymer which is expected to be soluble in $scCO_2$ based on the previous observations.[6] As a continuation of our earlier studies,[17,18] we report here in full the synthesis of these block copolymers by screened anionic polymerisation, as well as a detailed evaluation of the use of these stabilisers in the dispersion polymerisation of MMA in $scCO_2$.

Results and discussion

Synthesis of PMMA-*block*-PFMA block copolymers

The synthesis of the block copolymers was carried out using a modified version of the screened anionic polymerisation methodology (SAP).[19,20] One of the key advantages of this methodology is the ability to operate at temperatures close to 0 °C, whilst still maintaining a controlled polymerisation. This results from the shielding of the propagating species by a bulky lithium–aluminium alkyl complex at the enolate chain-end. A further advantage of this methodology is the pronounced yellow colour observed upon addition of monomer

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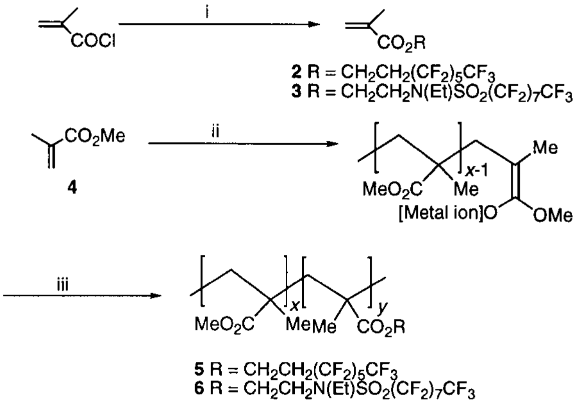


Scheme 1 Synthesis of fluorinated AB block copolymers. *Reagents and conditions*: i, ROH, **1** (R=$CH_2CH_2(CF_2)_5CF_3$), Et_3N, THF (76%); ii, Al^iBu_3, ^tBuLi, toluene, 1,3-bis(trifluoromethyl)benzene, 0 °C; iii, ester **2** or **3**, 1,3-bis(trifluoromethyl)benzene, −5 °C.

to the lithium–aluminium initiating species. The colour disappears upon consumption of the monomer, thus providing a useful indicator of the extent of polymerisation of the monomer, which is especially important in the synthesis of block copolymers. The polymerisation is 'living', and thus offers the ability to 'tune' the length of the PMMA as well as the PFMA block in the copolymers, according to specific requirements. The solubility problem associated with synthesis of block copolymers with relatively long fluorinated side chains noted by Krupers *et al.*[21,22] was overcome by the use of 1,3-bis(trifluoromethyl)benzene as a cosolvent with toluene.

The fluoroalkyl methacrylate **2** was prepared by esterification of methacryloyl chloride with the corresponding fluorinated alcohol **1** in the presence of triethylamine. The synthesis of diblock copolymers **5** using the SAP methodology *via* sequential addition of the respective monomers (MMA and **2**) is shown in Scheme 1. The results of the polymerisation are summarised in Table 1.

The initiator was prepared by mixing *tert*-butyllithium with an excess of Al^iBu_3 in a solution of toluene and 1,3-bis(trifluoromethyl)benzene (1:1 v/v) at 0 °C.[23,24] MMA was added dropwise and a yellow colour was observed. The polymerisation took place in minutes and the yellow colour disappeared. A sample of the polymerisation mixture was removed and quenched to give an accurate characterisation by GPC of the PMMA block. Subsequently, the fluorinated monomer, in a solution of 1,3-bis(trifluoromethyl)benzene, was added to the remaining 'living' polymer. The yellow colour reappeared and persisted for up to 45 min indicating a much slower reaction of this monomer in comparison with MMA. The properties of the block copolymers **5** synthesised using these optimum conditions are summarised in Table 1.

Table 1 Yields, ^1H NMR ratio of blocks, calculated and GPC molecular weight characterisation for AB block copolymers **5**

Entry	M_n PMMA block^a/10^{-3}	PMMA:PFMA^b (x:y in **5**)	Yield (%)^c	GPC $M_n^d/10^{-3}$	NMR $M_n^e/10^{-3}$
1	3.0	1:1.1	81	10.0	17.0
2	14.0	1:1.0	91	210.0	74.5
3	11.5	1:1.3	83	215.0	75.5

A mixture of ^tBuLi and Al^iBu_3 was used to initiate the polymerisation. A toluene:1,3-bis(trifluoromethyl)benzene ratio of 1:2.7 was used in all cases. [a]GPC analysis ($CHCl_3$, polystyrene standards) from extraction of sample of PMMA block after polymerisation of A block, followed by quenching with methanol. [b]The ratio of PMMA to PFMA blocks was estimated by the relative integrals in the ^1H NMR (500 MHz, $CDCl_3$) spectra; PFMA (CO_2CH_2–, δ 4.5 ppm), PMMA block (CO_2CH_3, δ 3.6 ppm). [c]Yield after precipitation into excess hexanes and MeOH. [d]Determined by GPC analysis ($CHCl_3$, polystyrene standards). [e]Calculated from M_n of A block and PMMA:PFMA ratio from ^1H NMR.

Table 2 Dispersion polymerisation of MMA in $scCO_2$ (10 cm^3 cell) at 285 bar and 70 °C with AIBN initiation [2.0 g MMA (20 w/v % in CO_2) and 10 mg AIBN (0.5 w/w % against MMA)]

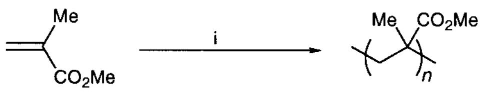
Entry	Surfactant **5** $M_n^a/10^{-3}$	PMMA:PFMA (x:y)	Wt% **5**^{b}	Yield (%)^c	M_n^e/ 10^{-3}	M_w/ M_n^e
1	—	—	0	16	22	2.5
2	17.0	1:1.1	1	79	129.0	3.1
3	74.5	1:1.0	1	91^d	160.0	3.4
4	75.5	1:1.3	1	84^d	340.0	2.7

[a]Calculated M_n from ^1H NMR (see Table 1). [b]Relative to the weight of MMA monomer. [c]Yield after precipitation into excess hexane. [d]Yield quoted without reprecipitation; free flowing powder obtained directly from the cell. [e]Determined by GPC analysis ($CHCl_3$, polystyrene standards).

Table 1 indicates that GPC-determined molecular weights of some fluorinated block copolymers can differ from the calculated values as determined from the ^1H NMR integrals of the copolymer. This is probably a result of the fact that measurements are based on comparisons against narrow polydispersity polystyrene reference standards. Copolymers having a large fluorinated block component tend to have different hydrodynamic volumes from those of the corresponding hydrogen-substituted analogues, partly owing to the rigidity of the PFMA block. In these experiments ^1H NMR spectroscopy provides a better estimate of molecular weight, by comparison of the integrals of the signal due to the methylene ester unit in the PFMA block with the integral of the signal due to the methyl ester unit in the PMMA block. We would not expect poly(methyl methacrylate) GPC reference standards significantly to alter the molecular weight determinations. Nevertheless, the GPC measurement is essential, since it gives a qualitative indication of the nature of the block copolymer. In particular, it shows that a narrow unimodal molecular weight distribution is observed in all cases.

Dispersion polymerisation of MMA in $scCO_2$

Effect of molecular weight of surfactant copolymers. Table 2 summarises the results of the radical dispersion polymerisation of MMA with AIBN initiation in $scCO_2$ using diblock copolymers **5** (Scheme 2). The stabilisers had varying molecular weights; however, the molar ratio of the PMMA to PFMA blocks was kept approximately constant. The polymerisations were carried out in a 10 cm^3 stainless steel reaction cell with a sapphire window at one end for viewing purposes. All the polymerisations appeared homogeneous initially, owing to the solubility of the monomer, initiator and block copolymer in the reaction medium. The need for a surfactant was demonstrated by polymerisation in the absence of the AB block copolymer. This resulted in low monomer conversion and low molecular weight PMMA (entry 1). In the absence of a surfactant, the polymer precipitated at an early stage, often leading to trapping of the stir bar and cessation of mixing. The results were somewhat variable due to the uncontrolled nature of the process, and polymer yields and molecular weights were always found to be low. In the presence of a small amount of AB block copolymer, the PMMA could be obtained from the reaction cell in both high yield and reasonable molecular weight. As the length of both anchoring PMMA



Scheme 2 Polymerisation of methyl methacrylate in $scCO_2$. *Reagents and conditions*: i, AIBN, $scCO_2$, 285 bar, 70 °C, 4 h, surfactant **5** or **6**.

block and the soluble PFMA block in the stabiliser was increased, there was a corresponding increase in yield and molecular weight and a narrowing of molecular weight distribution of the polymer product. When the lower molecular weight block copolymer was employed (entry 2), PMMA was obtained as solid blocks which had to be further reprecipitated to purify the product and obtain a powder. This suggested that the dispersions formed were initially stable, but that flocculation occurred as the reaction proceeded. When the molecular weight of the surfactant was increased, PMMA was obtained from the reaction cell as a free flowing powder, indicating that successful stabilisation of the colloidal dispersion occurred throughout the course of the reaction. A significant increase in the molecular weight of the PMMA product was observed when the relative block lengths in stabiliser **5** were varied (see entries 3 and 4). The stabiliser with the longer fluorinated block (entry 4) led to a higher molecular weight product. This is in agreement with studies involving the synthesis of cross-linked polymer microspheres in $scCO_2$, where it was found that surfactants with longer fluorinated blocks tended to give rise to better particle size control.[25] These results are also in accord with findings in conventional liquid solvents, where an increase in molecular weight of the polymeric dispersant increases the viscosity of the continuous phase and leads to a more efficient dispersion polymerisation.[26,27] This provides better stabilisation due to higher equilibrium amounts of stabiliser and a thicker layer of stabiliser on the particle surfaces.

Effect of monomer concentration. The dispersion polymerisation of MMA was also carried out at two different monomer concentrations (Table 3). Control reactions conducted in the absence of steric stabiliser at both monomer concentrations all afforded PMMA with low yields, low molecular weights and broad molecular weight distributions. Table 3 also summarises the results of the dispersion polymerisation of MMA carried out with a constant concentration of block copolymer **5** at both 20% w/v and 40% w/v MMA in CO_2.

The uniformity of the PMMA particle size was evaluated by scanning electron microscopy (SEM). The results indicated that both the particle diameter and the particle size distribution increased as the concentration of monomer was increased (Fig. 1). Particles ranging from 2–5 µm were obtained depending on the composition and quantity of the surfactant used.

In unstabilised reactions, increased monomer concentration led to increased polymer yield and molecular weight (Table 3, entries 1 and 2). The increase in yield is in agreement with studies on the unstabilised polymerisation of divinylbenzene mixtures in $scCO_2$.[28] In the presence of the diblock copolymer stabilizer, monomer concentration had little effect on either yield or molecular weight, which is consistent with the fact that these reactions were well-stabilised dispersion polymerisations. By contrast, the particle size was affected by monomer concentration, and higher monomer concentrations led to rather larger particles. The solvent power of the continuous phase in dispersion polymerisation plays an important role in determining particle size. The solvency of the continuous phase affects the point at which phase separation first occurs, and also the adsorption efficiency of the stabiliser.[29] In general, an increase in solvent strength tends to lead to decreased adsorption efficiency and the formation of fewer nuclei, thus giving rise to larger particles and broader particle size distributions. This is in agreement with our results for the stabiliser investigated. Nevertheless, this may not always be the case, since the precise effect of the monomer concentration on the adsorption efficiency for a particular stabiliser will depend strongly on the ratio of fluorinated to non-fluorinated blocks in the stabiliser. For example, MMA might be a non-solvent for a very highly fluorinated copolymer while being a good cosolvent for a less highly fluorinated copolymer of the same chemical structure.

Table 3 Effect of concentration of MMA on dispersion polymerisation of MMA in $scCO_2$ (10 cm^3 cell) at 285 bar and 70 °C with AB block copolymer **5** (x:y 1:1, M_n 74.5/10^{-3}), (0.5 wt% AIBN on monomer)

Entry	w/v % MMA[a]	w/w % **5**[b]	Yield (%)[c]	M_n[d]/ 10^{-3}	M_w/ M_n[d]	Particle size/ µm[e]
1	20	—	16	22.0	2.5	—
2	40	—	45	83.0	4.3	—
3	20	1.5	91	287.0	2.5	0.2–1[f]
4	40	1.5	87	257.0	2.9	2–5

[a] w/v % in CO_2. [b] Relative to the weight of MMA monomer. [c] Yield determined directly from the reaction cell without further reprecipitation except in the control experiment (reprecipitated into excess hexane). [d] From GPC analysis ($CHCl_3$, polystyrene standards). [e] Scanning electron microscopy. [f] Agglomeration.

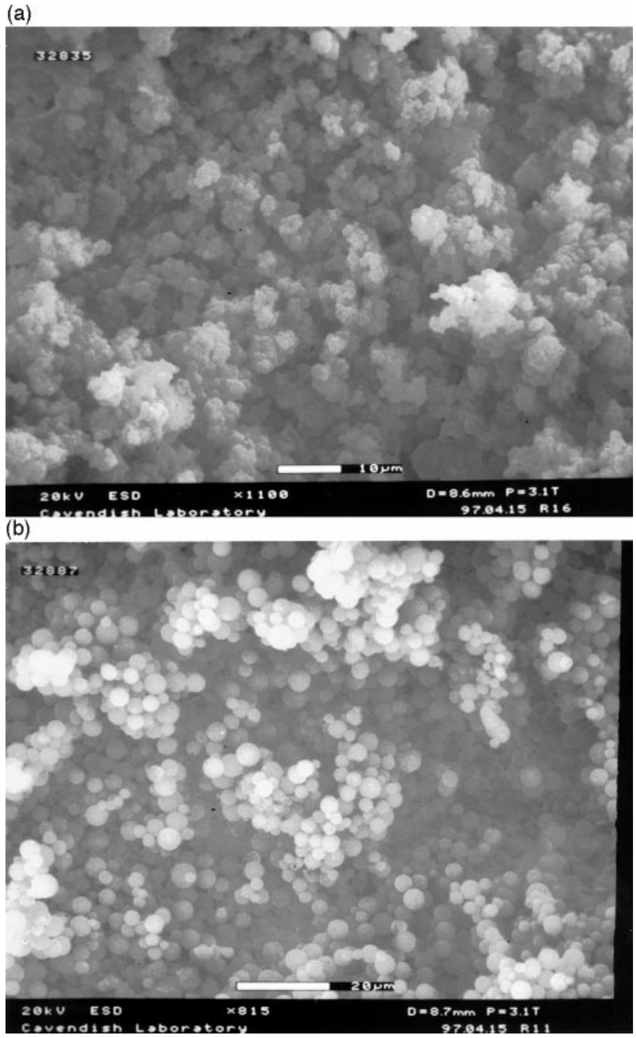


Fig. 1 Effect of monomer concentration on morphology of PMMA particles; (a) 20% MMA; (b) 40% MMA. See Table 3, entries 3 and 4 respectively.

Effect of stabiliser concentration. The effect of the surfactant concentration on the polymerisation was investigated using block copolymer **5** as stabiliser. The experimental conditions for monomer and initiator concentrations, temperature and initial pressure were kept constant. The results for the polymerisations are summarised in Table 4.

The results show that increasing the concentration of stabiliser resulted in an increase in molecular weight of the PMMA produced. This is indicative of a more efficient stabilis-

Table 4 Dispersion polymerisation of MMA in CO_2 at 285 bar and 70 °C with AIBN initiation with different levels of block copolymer **5** (x:y 1:1, M_n 74.5/10^{-3}) [2.0 g MMA (20% w/v in CO_2) and 10 mg AIBN (0.5 w/w % against MMA)]

Entry	w/w % **5**[a]	Yield (%)[b]	M_n[c]/10^{-3}	M_w/M_n[c]
1	0	16	22.0	2.5
2	1	92	160.0	3.4
3	1.5	91	287.0	2.5
4	2	88	389.0	2.5
5	4	91	375.0	2.3

[a] Relative to the weight of MMA monomer. [b] Yield determined directly from the reaction cell without further reprecipitation except in the control experiment (reprecipitated into excess hexane). [c] From GPC analysis ($CHCl_3$, polystyrene standards).

ation of the dispersed particles. At low concentrations of surfactant (1% w/w relative to monomer) a broader molecular weight distribution was observed. With only a limited amount of steric stabiliser to achieve coverage of the particle surface, a degree of coalescence resulted, probably causing broadening of the molecular weight distribution. Dispersion polymerisations that were conducted with block copolymer concentrations above 1% w/w formed stable dispersions throughout the entire reaction. Increasing the stabiliser concentration above 2% w/w had little effect, probably because complete coverage of the particle surfaces had been achieved at this concentration.

An increase in stabiliser concentration will increase the viscosity of the continuous phase and the rate of physical adsorption of the anchoring components.[30] Both of these changes reduce the extent of aggregation and thus lead to a reduction in particle size, as was observed with stabilisers of this type in the heterogeneous polymerisation of divinylbenzene in $scCO_2$.[28] In all of the reactions shown here, the addition of stabiliser results in significant enhancements in conversion and molecular weights of the resulting PMMA.

Block copolymers based on commercially available monomers. Fluorinated monomers based on fluoroalkyl alcohols are relatively expensive. Block copolymers **6** were synthesised using less expensive, commercially available monomer. The AB block copolymers were synthesised using *N*-ethyl(perfluorooctylsulfonamido)ethyl methacrylate **3** (FOSEMA) as the fluorinated monomer using the standard methodology. The length of the PMMA block was kept constant whilst the length of the PFMA block was varied. Table 5 lists the surfactants prepared and their use as stabilisers in the dispersion polymerisation of MMA in $scCO_2$. Again, by increasing the length of the PFMA block, better stabilisation occurred throughout the course of the polymerisation and PMMA could be obtained in high yields and with high molecular weights. At a given concentration, stabiliser **6** was slightly less effective than stabiliser **5**. Stabiliser **6**, particularly the less highly fluorinated copolymer, was found to be rather less readily soluble in CO_2 (Table 5, entry 2). The more highly fluorinated stabiliser (entry 3) was more readily soluble in CO_2, and was also more effective in the dispersion polymerisation.

Table 5 Dispersion polymerisation of MMA in $scCO_2$ at 285 bar and 70 °C with AIBN initiation [2.0 g MMA (20% w/v in CO_2) and 15 mg AIBN (0.75% w/w against MMA)] in the presence of block copolymer **6** as surfactant

Entry	Surfactant **6** M_n[a]/10^{-3}	PMMA:PFMA (x:y)	w/w % **6**[b]	Yield (%)[c]	M_n[a]/ 10^{-3}	M_w/ M_n[a]
1	—	—	—	46	88.0	3.6
2	30.3	1.0:0.56	2.5	66	132.0	2.5
3	55.0	1.0:0.83	2.5	91	200.0	2.6

[a] Determined by GPC analysis ($CHCl_3$, polystyrene standards). [b] Relative to the weight of MMA monomer. [c] Yield after precipitation into excess hexane.

Conclusions

In summary, we have developed a highly controlled synthesis of fluorinated AB block copolymers. The virtue of this method is that the length and therefore the 'CO_2-philicity' of the fluorinated block can be tuned through a wide range of ratios. Also, since SAP is a 'living polymerisation', a broad range of well-defined molecular weights can be obtained. We have demonstrated that these block copolymers can act as stabilisers in the dispersion polymerisation of MMA in $scCO_2$, leading to high yields and molecular weights. Moreover, the higher molecular weight and more highly fluorinated block copolymers are considerably better surfactants, which demonstrates further the necessity for precise control in the surfactant synthesis. By systematic evaluation of the parameters in the dispersion polymerisation, discrete polymer particles can be obtained.

Experimental

Materials and characterisation

MMA (Aldrich) and 1,3-bis(trifluoromethyl)benzene (Aldrich) were distilled from calcium hydride and stored over activated 4 Å molecular sieves at 4 °C. Methacryloyl chloride (Aldrich) was distilled prior to use. 1H,1H,2H,2H-Perfluorooctan-1-ol (Fluorochem) and *N*-ethyl(perfluorooctylsulfonamido)ethyl methacrylate were used as received. Gel permeation chromatography (GPC) was performed with a Polymer Laboratories PLgel 5 μ mixed-C column, a Waters 501 HPLC pump and either an ICI LC UV–VIS detector or an HP 1047A refractive index detector, and calibrated against polystyrene standards. ^1H NMR spectra were recorded on a Bruker DRX-500 (500 MHz) spectrometer and ^{13}C NMR spectra were recorded on a Bruker AC-400 (100 MHz) spectrometer.

Synthesis of 1H,1H,2H,2H-perfluorooctyl methacrylate *2*

A typical esterification reaction is described. To a solution of 1H,1H,2H,2H-perfluorooctan-1-ol **1** (8.0 g, 36.3 mmol) and triethylamine (6.6 cm^3, 0.047 mol) in THF (50 cm^3), was added freshly distilled methacryloyl chloride (5.2 cm^3, 0.054 mmol). Formation of a white solid (triethylammonium chloride) was observed on addition of methacryloyl chloride. The mixture was stirred at room temperature for 3 h. The reaction mixture was filtered through Celite and ether (150 cm^3) was added to the filtrate. The organic layer was washed with saturated aq. $NaHCO_3$ (150 cm^3), 2 M HCl (150 cm^3) and brine (150 cm^3). The aqueous portions were extracted successively with another portion of ether (150 cm^3). The combined ethereal layers were dried ($MgSO_4$) and the solvent was removed by rotary evaporation to yield the crude ester **2**. Flash column chromatography on silica gel, eluting with hexane, hexane–ether 95:5 and kugelrohr distillation (100 °C, 0.1 mmHg), gave *1H,1H,2H,2H-perfluorooctyl methacrylate* **2** as a colourless liquid (11.8 g, 76%); R_f 0.42 ether–hexane 1:9; ν_{max}(film)/cm^{-1} 1736 (C=O), 1639 (C=C), 1170 (C–O); δ_H (500 MHz, $CDCl_3$) 6.13 (1H, s, C=C*H*), 5.60 (1H, s, C=C*H*), 4.45 (2H, t, *J* 6.5, CO_2CH_2), 2.51 (2H, tt, *J* 18.0, 6.5, CH_2CF_2), 1.98 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 166.9 (C=O), 135.7 (C), 126.3 (CH_2), 118.6 (m, CF_2), 117.5 (m, CF_2), 115.7 (m, CF_2), 112.9 (m, CF_2), 111.0 (m, CF_2), 108.6 (m, CF_2), 56.5 (CH_2, t, *J* 4.2, CO_2CH_2), 30.5 (CH_2, t, *J* 21.7, CH_2CF_2), 18.0 (CH_3); *m*/*z* (EI) 432 [(M^+), 13%], 149 (50), 104 (20), 69 (100), 57 (20), 41 (52). [Found: (M^+) 432.0393, $C_{12}H_7O_2F_{15}$ requires *M* 432.0393].

General procedure for the synthesis of AB block copolymers of type 5.

To a solution of Al^iBu_3 (1.0 M in toluene, 0.5 cm^3, 0.5 mmol) in toluene (2.5 cm^3) and 1,3-bis(trifluoromethyl)benzene (2.5 cm^3) was added ^{t}BuLi (1.6 M in hexane, 0.15 cm^3, 0.2 mmol) at 0 °C under N_2. The resulting solution was allowed to stir for 5 min. MMA (0.5 cm^3, 5.0 mmol) was added dropwise at 0 °C. A pronounced yellow colour was observed initially, but the reaction mixture gradually became colourless after a few minutes. When this had occurred, half of the reaction mixture (2.7 cm^3) was removed by syringe and precipitated into excess MeOH. A solution of 1H,1H,2H,2H-perfluorooctyl methacrylate **2** (1.1 g, 2.5 mmol) in 1,3-bis(trifluoromethyl)benzene (3.0 cm^3) was then added dropwise to the remaining reaction mixture. A pronounced yellow colour was again observed and the reaction mixture was stirred at 0 °C for 30 min. A few drops of methanol were added to terminate the reaction and the polymer was precipitated out in excess hexane. After redissolving in CH_2Cl_2, the polymer was reprecipitated out into excess MeOH, collected by filtration and dried *in vacuo*. The AB block copolymer was obtained as a white powdery solid (1.10 g, 91%); ν_{max}(KBr)/cm^{-1} 1734 (C=O), 1174 (C–O); {M}: methyl methacrylate block, {F}: fluorinated methacrylate block, δ_H (500 MHz, $CDCl_3$) 4.60–3.80 (2H{F}, br s, CH_2), 3.61 (3H{M}, s, CH_3), 2.70–2.20 (2H{F}, br s, CH_2), 2.15–1.7 (2H{M}, 2H{F}, br m, CH_2), 1.22–0.80 (3H{M}, 3H{F}, br m, α-CH_3); from integrals in the ^{1}H NMR spectra, the ratio of the PMMA block (CO_2CH_2-, δ 4.60–3.80 ppm) to the PFMA block (CO_2CH_3, δ 3.6 ppm) was 1.0 : 1.0.

General procedure for the polymerisation of MMA in $scCO_2$ (10 cm^3 cell) in the presence of block copolymers

All supercritical polymerisations were carried out in a 10 cm^3 stainless steel high pressure reactor equipped with a sapphire window to view the contents of the cell. The reactions were stirred by a magnetic stirrer bar. Carbon dioxide (B.O.C. 99.995%) was passed through an Oxisorb catalyst (MG Gas Products) to remove traces of oxygen. The carbon dioxide was delivered to the reaction cell using a Pickel PM101 air driven pump at the desired pressure. The system pressure was measured by a pressure transducer (A105, RDP Electronics) and displayed on a digital display (E308, RDP Electronics). The temperature inside the cell was measured by an industrial insulated thermocouple (Type K, RS Electronics) and displayed on a temperature indicator (T200, RS Electronics). The reactor was heated with an electrical heating tape wrapped around the exterior of the cell.

Degassed methyl methacrylate and AIBN were added under N_2 to the stainless steel cell (10 cm^3) containing the specified amount of AB block copolymer, and which had been previously purged with N_2. The cell was initially pressurised with CO_2 and then gradually heated to 70 °C to obtain the desired pressure. The reaction mixture was stirred under these conditions for 4 h. The cell was cooled to room temperature and the CO_2 was vented into CH_2Cl_2. The cell was opened to give poly(methyl methacrylate) as a powdery white solid.

Acknowledgements

We thank EPSRC for financial support of this work and provision of the Swansea Mass Spectroscopy Service, ICI plc for a Strategic Research Fund Award (TMY), the Ramsay Memorial Trustees (Fellowship to AIC), the UK Committee of Vice-Chancellors and Principals for an ORS award, the Cambridge Commonwealth Trust for a bursary, and Zeneca Agrochemicals for a CASE award (WPH). We thank Professor M. Poliakoff and Dr S. M. Howdle for help in the design of supercritical apparatus, Dr J. H. G. Steinke and Dr P. L. Taylor for their interest in this work.

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Paper 9/01105F