Synthesis of fluorinated block copolymers and their application as novel polymerisation surfactants in supercritical carbon dioxide

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Screened anionic copolymerisation of methyl methacrylate with the perfluoroalkyl methacrylates 2 affords well-defined AB block copolymers 4–6, which serve as effective surfactants in the dispersion polymerisation of methyl methacrylate in supercritical carbon dioxide.

Fluorinated polymers possess interesting properties such as low surface energy, toughness, good chemical resistance and high temperature stability.[1–3] It is consequently expected that AB block copolymers consisting of a flexible poly(methyl methacrylate) (PMMA) block and a more rigid poly(perfluoroalkyl methacrylate) (PFMA) block will also exhibit interesting properties, and that they may have potential uses in specialist applications. The 'screened' anionic polymerisation (SAP) method has been developed to obtain well-defined block copolymers of methyl methacrylate (MMA) derivatives with narrow molecular weight distribution.[4] The key advantage of this methodology is the ability to operate at temperatures close to 0 °C while maintaining a controlled polymerisation, which results from the 'shielding' of the propagating terminus from unwanted side reactions by a bulky lithium–aluminium alkyl complex at the enolate chain-end. We report the use of a modified SAP methodology for the synthesis of AB block copolymers, consisting of a PMMA block and a PFMA block, as well as their application as novel surfactants in the dispersion polymerisation of methyl methacrylate in supercritical carbon dioxide (scCO2).[5]

The syntheses of three AB block copolymers 4, 5 and 6 with different lengths of perfluoroalkyl side chains in the PFMA block are shown in Scheme 1. The fluorinated monomers 2 were synthesised by esterification of methacryloyl chloride 1 with the corresponding fluorinated alcohols in the presence of triethylamine. Table 1 summarises the polymerisation results. The SAP initiator was prepared by mixing *tert*-butyllithium with (2,6-di-*tert*-butyl-4-methylphenoxy)diisobutylaluminium [Al(BHT)-Bu$^i_2$] 3 in toluene at 0 °C. A toluene solution of methyl

methacrylate (MMA) was added dropwise to the initiator and polymerisation took place within minutes. Directly afterwards, a toluene solution of fluorinated monomer 2 was added to the reaction mixture. This resulted in ill-defined block copolymers for some examples (*e.g.* entry 3) where the proportion of 2b incorporated into the PFMA block was less than expected, as indicated by the yield and ^{1}H NMR analysis. Gel permeation chromatography (GPC) against polystyrene standards revealed that the sample contained a copolymer with broad molecular weight distribution, whereas a sample of the PMMA block obtained before addition of 2b revealed a polymer composition of low polydispersity ($Mw/Mn \leqslant 1.3$). This indicated that loss of control occurred after addition of 2b, which is probably a result
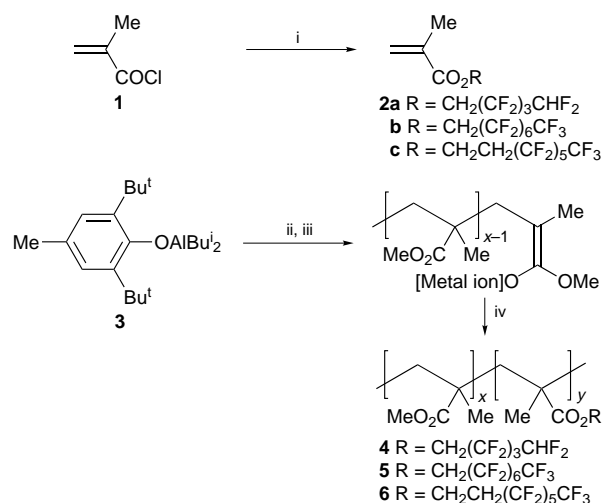

Scheme 1 *Reagents and conditions*: i, ROH, Et₃N, THF, 69–79%; ii, Bu^{t}Li, PhMe, 0 °C; iii, MMA, PhMe; iv, 2, PhMe, 1,3-bis(trifluoromethyl)benzene, −10 °C

Table 1 Synthesis of AB block copolymers 4, 5 and 6[a]

Entry	2 (mmol)	Solvent[b]	Polymer	PMMA : PFMA[c]	Yield[d] (%)	M_n[e]/10^{-3}	M_w/M_n[e]
1	2a (5.9)	1:0	4′	1.0 : 2.1	76	20.0	1.2
2	2a (5.8)	3:1	4″	1.0 : 2.3	83	19.0	1.2
3	2b (1.9)	1:0	5′	1.0 : 0.3	45	f	f
4	2b (1.9)	4:3	5″	1.0 : 0.6	86	217	1.1
5	2c (2.5)	1:3	6′	1.0 : 1.1	81	17	1.5
6	2c (3.5)	1:15	6″	1.0 : 1.3	72	197	1.3

[a] To initiate the polymerisation a mixture of *tert*-butyllithium (0.17 mmol) and Al(BHT)Bu$^i_2$ (0.7 mmol) was used. In each experiment 2.8 mmol of MMA were used except entry 5 (2.5 mmol). [b] Ratio (v/v) toluene : 1,3-bis(trifluoromethyl)benzene. [c] Determined from ^{1}H NMR spectroscopy. [d] Yields quoted after two reprecipitations in hexane. [e] From GPC analysis (CHCl₃, polystyrene standards). [f] GPC assay revealed two peaks: (i) M_n 16400 M_w/M_n 1.3, (ii) M_n 245000 M_w/M_n 2.0.
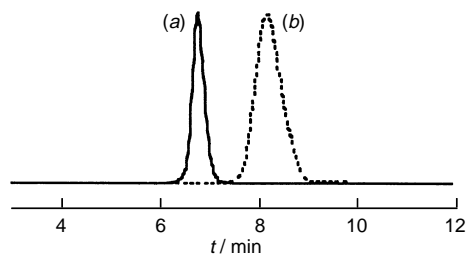
Fig. 1 GPC trace (polystyrene standards, CHCl$_3$) of a sample of (*a*) **5″** (M_n 218 000, M_w/M_n 1.1) and (*b*) the PMMA block before addition of **2b** (M_n 9300, M_w/M_n 1.3)

of the insolubility of the propagating fluorinated block. In the case of the copolymer **4′** with a shorter perfluoroalkyl side chain, this solubility problem was less apparent. Good yields of **4′** were obtained, and the polydispersity was relatively narrow, even for samples with a high proportion of PFMA in relation to the PMMA block (entry 1). The solubility problem could be overcome by the use 1,3-bis(trifluoromethyl)benzene as a co-solvent with toluene, which enabled the preparation of block copolymer **5″** with a high proportion of PFMA block (entry 4). The GPC chromatogram of copolymer **5″** is shown in Fig. 1. The chromatogram of a sample of PMMA obtained before addition of **2b** is also shown. Both unimodal traces with narrow polydispersity reveal that a controlled polymerisation is maintained throughout the reaction.†

Block copolymers can exhibit micelle-like aggregation if they are dissolved in a solvent which is more selective towards one of the blocks.[6] Fluorinated homopolymers have been known to be very soluble in both liquid CO$_2$ and scCO$_2$.[7] In the case of the AB block copolymers described above, the PFMA block will have a much higher solubility in scCO$_2$ compared with the PMMA block, and may thus be employed as a stabiliser or surfactant in a dispersion polymerisation.[7] In preliminary studies we have polymerised MMA under free radical conditions in scCO$_2$ using copolymers **4** and **6** as surfactants (Scheme 2).[8] These results demonstrate that these surfactants play an important rôle in stabilising a dispersion of the growing PMMA chain in scCO$_2$. In the presence of **4″** (Table 2, entry 2), both the yield and molecular weight (M_n) of the polymer are significantly higher than observed in the control experiment without surfactant (Table 2, entry 1). However, elongation of the fluorinated side-chain improved these results even more (Table 2, entry 3). The effect of the molecular weight of the surfactant, where there is an increase of the length of the different blocks, is illustrated by comparing the surfactant **6′** with **6″**. In the latter case (Table 2, entry 4) we were able to obtain PMMA as a free flowing powder together with further increase in molar mass.

In summary, we have developed a highly controlled synthesis of fluorinated AB block copolymers. The ability to vary the side chain as well as to 'tune' the length of the different blocks in
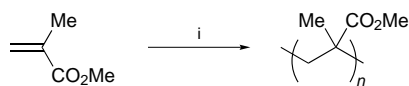
Table 2 Radical polymerisation of MMA (1.2 M) with AIBN (2 wt%) as initiator in scCO$_2$ with and without block copolymers as surfactant

Entry	Surfactant (1 wt%)	Yield^a (%)	$M_n{}^b/10^{-3}$	$M_w/M_n{}^b$
1	—	22	12.0	2.0
2	**4″**	56	38.0	2.2
3	**6′**	69	77.4	3.0
4	**6″**	72^c	81.9	2.3

^{a} Yields quoted after two reprecipitations in hexane. ^{b} GPC analysis (CHCl$_3$, polystyrene standards) confirmed by multiple angle light scattering analysis in THF. ^{c} Yield quoted without reprecipitation; free-flowing powder obtained.

these block copolymers, according to specific requirements, is an advantage of the synthetic route described. Moreover, the improved stabilising efficiency of block copolymer **6″**, compared with block copolymer **4″**, in the dispersion polymerisation of MMA in scCO$_2$ demonstrates the applicability of this synthetic methodology. We shall describe the power of the tunability of the surfactant in a forthcoming publication.

Footnotes and References

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† It is possible that the molecular weight obtained for **4**, **5** and **6** is overestimated, owing to the rigidity of the PFMA block compared with the flexible polystyrene reference standards used.

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8 During the course of our study the use of fluorinated block copolymers in the dispersion polymerisation of styrene (see D. A. Canelas, D. E. Betts, J. M. DeSimone, *Macromolecules*, 1996, **29**, 2818) as well as the use of fluorinated graft copolymers in the dispersion polymerisation of MMA in scCO$_2$ was reported (see C. Lepilleur and E. J. Beckman, *Macromolecules*, 1997, **30**, 745).

Scheme 2 *Reagents and conditions*: i, AIBN, scCO$_2$, 285 bar, 70 °C, 5 h, **4** or **6**