ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 10626–10636

polymer

www.elsevier.com/locate/polymer

# High molecular weight graft stabilisers for dispersion polymerisation of vinylidene fluoride in supercritical carbon dioxide: the effect of architecture

Hongyun Tai, Wenxin Wang, Steven M. Howdle*

*School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK*

Received 28 May 2005; received in revised form 6 September 2005; accepted 7 September 2005
Available online 26 September 2005

## Abstract

A group of high molecular weight graft stabilisers, both fluorinated and non-fluorinated, were synthesised by thermal ring-opening esterification of anhydride copolymers. These included poly(methyl vinyl ether-*alt*-maleic anhydride) and poly(maleic anhydride-octadecene) and were reacted with alcohols, including 1H,1H,2H,2H-perfluorooctanol, 1H,1H,2H,2H-perfluoro-dodecanol and 1-octanol. The stabilisers were fully characterised by $^{1}$H, $^{19}$F and $^{13}$C nuclear magnetic resonance, diffuse reflectance Fourier transform infrared spectroscopy, and thermal analysis. Their phase behaviour in supercritical carbon dioxide (scCO$_2$), vinylidene fluoride (VDF), and a mixture of scCO$_2$/VDF was also studied using a variable volume view cell. Each stabiliser was tested for the dispersion polymerisation of VDF in scCO$_2$. The effect of the stabiliser architecture on the molecular weight and morphology of the poly(vinylidene fluoride) (PVDF) polymer product was investigated. Steric stabilisation effects were observed. Gel permeation chromatography and scanning electron microscopy were used for the characterisation of the molecular weight and morphology of PVDF polymers.

*Keywords:* Poly(vinylidene fluoride) (PVDF); Supercritical carbon dioxide (scCO$_2$); Dispersion polymerisation

## 1. Introduction

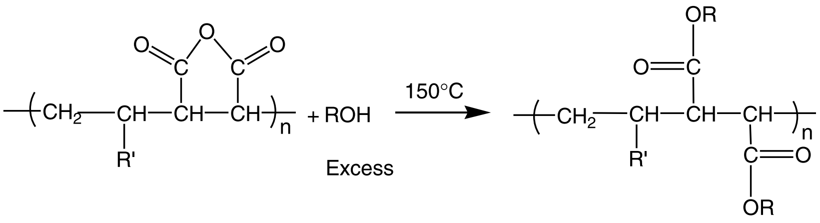
Carbon dioxide (CO$_2$) is inexpensive, non-toxic, non-flammable, and readily available in high purity from a variety of sources. In recent years, supercritical carbon dioxide (scCO$_2$) has generated much interest in the polymer synthesis and polymer materials processing communities as an attractive alternative solvent [1–5]. Dispersion polymerisations in scCO$_2$ lead to polymer products of higher molecular weight, in greater yield and with better particle morphology compared to a surfactant free precipitation polymerisation [3]. To accomplish successfully a dispersion polymerisation, specially designed stabilisers have to be used. These stabilisers should have both CO$_2$-philic and polymer-philic portions to allow them to stabilise the reaction system. Typical stabilisers reported so far have been fluorinated [4,5] and siloxane [6,7] based homopolymers (e.g., poly(1,1-dihydroperfluorooctyl acrylate) (poly(FOA)) [4], polydimethylsiloxane (PDMS) macromonomers [8]), block or graft copolymers [9–11] and reactive macromonomers [8]. Beckman et al. reported that poly(ether-carbonate) was found to be the most soluble hydrocarbon polymer in scCO$_2$ so far [12]. This has raised much interest in the investigation of non-fluorous and non-siloxane based CO$_2$-soluble stabilisers for the use in the dispersion polymerisations in scCO$_2$. In some cases the polymer product itself plays a role as a stabiliser with no need for additional stabilisers [13].

Poly(vinylidene fluoride) (PVDF) possesses excellent thermal, chemical and weather stability and is used primarily for pipes, valves, coatings and films as well as being an acceptable biomaterial [14]. The conventional methods for PVDF preparation are by aqueous suspension and emulsion polymerisations, which both generate a large quantity of waste water and can require a substantial quantity of energy to dry the polymer [15]. Using scCO$_2$ as the reaction medium, polymer products can be isolated from the reaction mixture by a simple depressurisation, resulting in a dry polymer product. This eliminates the necessity for energy-intensive drying procedures. There are some publications on the investigation of free radical (co)polymerisation of VDF by aqueous emulsion and suspension techniques [16–20]. However, there are only

---

* Corresponding author. Tel.: +44 115 951 3486; fax: +44 115 951 3058.
*E-mail address:* steve.howdle@nottingham.ac.uk (S.M. Howdle).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.09.028



**A** **B** **C**

Fig. 1. The synthetic route of graft stabilisers, where $R'$ = $-OCH_3$ or $-CH_2(CH_2)_{14}CH_3$; R = $-CH_2CH_2(CF_2)_5CF_3$, $-CH_2CH_2(CF_2)_9CF_3$ or $-(CH_2)_7CH_3$.

a few publications regarding the polymerisation of VDF in $scCO_2$. A continuous polymerisation of VDF in $scCO_2$ has been reported [21–23], as well as the dispersion polymerisation of VDF using a range of VDF-based copolymers as stabilisers [11]. However, no distinct, spherical particles were obtained. In addition, Shoichet and coworkers investigated the copolymerisation of VDF and vinyl acetate in $scCO_2$ by a free radical mechanism without the use of a surfactant [13]. A tacky solid copolymer was obtained while the copolymer contained less than 23 mol% VDF. We have reported elsewhere that commercially available PDMS monomethacrylate (PDMS-ma) has a clear effect on the homopolymerisation of VDF in $scCO_2$, leading to a high molecular weight product with a broad molecular weight distribution (MWD), and primary particles (200–500 nm) that coagulate to form larger uniform coarse particles (200–500 μm) [24].

Recently, we reported that a fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) (F-*g*-PMVE-MA) was an effective stabiliser for the polymerisation of VDF in $scCO_2$ [25]. In this paper, we explore in detail the effect of the architecture of this type of fluorinated graft copolymers on the polymerisation of VDF in $scCO_2$. The common structure of these fluorinated graft stabilisers is shown in Fig. 1. By the addition of fluorinated graft chains with different chain lengths (R), varying the degree of graft chain incorporation, and the use of a longer polymer backbone and various pendant group ($R'$), a group of fluorinated graft stabilisers was synthesised and fully characterised. In addition, a non-fluorinated alcohol (1-octanol) was also used to prepare a non-fluorinated graft stabiliser (NFGS). All of the stabilisers were tested in the dispersion polymerisations of VDF in $scCO_2$.

## 2. Experimental section

### 2.1. Synthesis of stabilisers

Stabilisers were synthesised by a thermal ring opening esterification [26] (Fig. 1) using the anhydride **A**, including poly(methyl vinyl ether-*alt*-maleic anhydride (PMVE-MA) with a number-average molecular weight $M_n = 79.8$ or 1130 kg/mol (Aldrich Chemical Company), or poly(maleic anhydride-octadecene) (PMA-OD) ($M_n = 30$–$50$ kg/mol, Aldrich Chemical Company). A range of alcohol **B**, including 1H,1H,2H,2H-perfluorooctan-1-ol (PFOL) (purity 97%, Lancaster Synthesis) or 1H,1H,2H,2H-perfluoro-dodecanol (PFDL) (purity 97%, Lancaster synthesis) or 1-octanol (GC grade, 99%, Aldrich Chemical Company) were used. All were used as received. Reactions were carried out at various mole ratios of A and B at 150 °C for various periods of time (as stated in Table 1) in a parallel synthesiser (Radleys Discovery Technologies) assembled with 12 glass reaction tubes ($20 \times 150$ mm$^2$, 50 ml). After removal of the excess alcohol under vacuum, brown brittle (FGS-I-a, FGS-I-b, FGS-I-c, FGS-II, FGS-IV) or tacky (FGS-III and NGFS) solid products were obtained.

### 2.2. Characterisation of stabilisers

$^1$H NMR, $^{19}$F NMR and $^{13}$C NMR were performed for the stabilisers and the starting materials using a Bruker 300 MHz spectrometer. Infrared analysis for the fluorinated graft stabilisers and the starting materials (PMVE-MA and PMA-OD) was carried out using a Perkin–Elmer system 2000 FTIR spectrometer equipped with a diffuse reflectance infrared spectroscopy (DRIFTS) attachment (Spectratech). Thermal analysis of stabilisers by differential scanning calorimetry

Table 1
Preparation of the graft stabilisers

| Stabilisers | Anhydride ($M_n$, kg/mol) A | Alcohol B | A:B (mol ratio) | Reaction time (days) | Degree of grafting[a] |
|---|---|---|---|---|---|
| FGS-I-a | PMVE-MA (79.8) | PFOL | 1.0:1.0 | 5 | 1.3 |
| FGS-I-b | PMVE-MA (79.8) | PFOL | 1.0:2.0 | 5 | 1.8 |
| FGS-I-c | PMVE-MA (79.8) | PFOL | 1.0:4.0 | 10 | 2.0 |
| FGS-II | PMVE-MA (1,130) | PFOL | 1.0:4.0 | 10 | 1.9 |
| FGS-III | PMA-OD (30–50) | PFOL | 1.0:4.0 | 10 | 1.3 |
| FGS-IV | PMVE-MA (79.8) | PFDL | 1.0:4.0 | 10 | –[b] |
| NFGS | PMVE-MA (79.8) | 1-Octanol | 1.0:4.0 | 10 | 1.6 |

[a] Determined by $^1$H NMR analysis. Note that PMVE-MA is poly(methyl vinyl ether-*alt*-maleic anhydride) copolymer; PFOL is 1H,1H,2H,2H-perfiuorooctanol; PFDL is 1H,1H,2H,2H-perfluoro-dodecanol; PMA-OD is poly(maleic anhydride-octadecene).

[b] The value was not obtained by $^1$H NMR because a suitable deuterated solvent for this stabiliser could not be found.

(DSC) and thermal gravimetric analyser (TGA) were performed using TA Instruments MDSC 2920 and TGA 2950. For DSC, samples weighing about 6 mg were closed in aluminium pans, which were heated at a rate of 5 °C/min from −50 to 100 °C under nitrogen atmosphere; for TGA, samples were heated at a rate of 50 °C/min at resolution-3 in nitrogen atmosphere from 25 °C up to a maximum temperature of 800 °C.

### 2.3. Phase behaviour of stabilisers

The phase behaviour of the stabilisers in pure $scCO_2$, as well as in pure VDF and a mixture of VDF/$scCO_2$ was studied using a hydraulic variable volume view cell [27] equipped with a sapphire window and a moving piston fabricated completely from sapphire. The maximum pressure for the view cell is 6000 psi (40.82 MPa). The stabiliser (0.26 g, 6.5 wt% with respect to (wrt) VDF monomer, 1.2 wt% wrt $CO_2$) was placed in the view cell, which was then sealed. $CO_2$ (21 g) was transferred into the cell through a sample vessel cylinder (80 ml, maximum pressure 1800 psi (12.24 MPa)). The cell was heated to the desired temperature 45 °C) and equilibrated for 5 min. Then by gradually decreasing its volume, the pressure of the cell was raised above the point at which the system became homogeneous (one phase). After equilibration, the pressure was decreased slowly by withdrawing the piston and increasing the cell volume until the system became visibly heterogeneous (two phases) and it was no longer possible to see the piston through the window. The pressure and temperature at this point was defined as the cloud point for this specific mixture of the stabiliser and $CO_2$. By the same procedure, cloud points were obtained at various temperatures (55, 65, 75 and 85 °C). Cloud point curves of the stabilisers in pure VDF and a mixture of VDF/$CO_2$ at various ratios were also collected by the same procedure.

### 2.4. Polymerisations of VDF in $scCO_2$

The initiator for the polymerisations of VDF, diethyl peroxydicarbonate (DEPDC), was synthesised according to the published methods [28]. The final product solution was approximately 10 wt% DEPDC in 1,1,2-trichlorotrifluoroethane (Freon 113), and stored at −15 °C. VDF monomer was donated by Solvay Research, Belgium, and used without further purification. $CO_2$ (SFC grade) was purchased from BOC and used without further purification.

Polymerisations were carried out in a 60 ml stainless steel autoclave [24] at 55 °C, with stirring at 100 rpm, an initial vessel pressure of 4000 psi (27.21 MPa), concentration of VDF monomer [M] as 9.8 mol/l, concentration of initiator [I] as 1.5 mmol/l, and concentration of stabiliser [S] as 0.52 wt% (weight/weight relative to VDF monomer). In all cases, the reactions were deliberately terminated when the pressure in the autoclave fell by 300 psi (2.04 MPa); the point at which we found that the solid contents in autoclave approaches ca. 33 g/l. The carbon dioxide was vented slowly and the autoclave opened.

### 2.5. Characterisation of PVDF polymers

Gel Permeation Chromatography (GPC) was performed at 80 °C using a K-501 HPLC pump with two PLgel 5 μm MIXED-C columns (300×7.5 $mm^2$, particle size 5 μm, with its linear calibration range of $M_w$ 200–2,000,000 g/mol), 1 PLgel 5 μm Guard column (50×7.5 $mm^2$, particle size 5 μm) and refractive index detector. *N*,*N*-Dimethylformamide (DMF) modified with 0.1 M lithium bromide (LiBr) was used as the solvent. DMF is a polar solvent and PVDF is a polar polymer. Therefore, there is a dipole interaction that occurs, causing artificial shoulders to appear on the high molecular weight end of the distribution. This interaction is eliminated by the addition of LiBr. The calibration was accomplished at 80 °C with narrow MWD standards of poly(methyl methacrylate) (PMMA) (Polymer Laboratories Ltd).

The morphology of the PVDF product was determined using a Philips XL30 ESEM-FEG machine. DSC analysis for PVDF polymers was performed using TA Instrument MDSC 2920 following standard procedures (ASTM D3418-99). Samples weighing about 6 mg were closed in aluminium

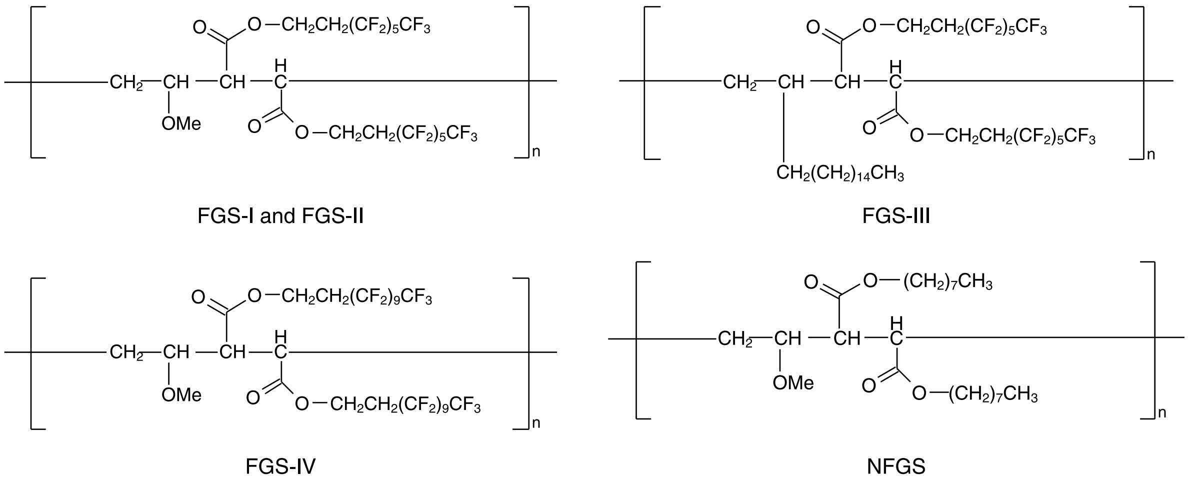


Fig. 2. Structures of the graft stabilisers.

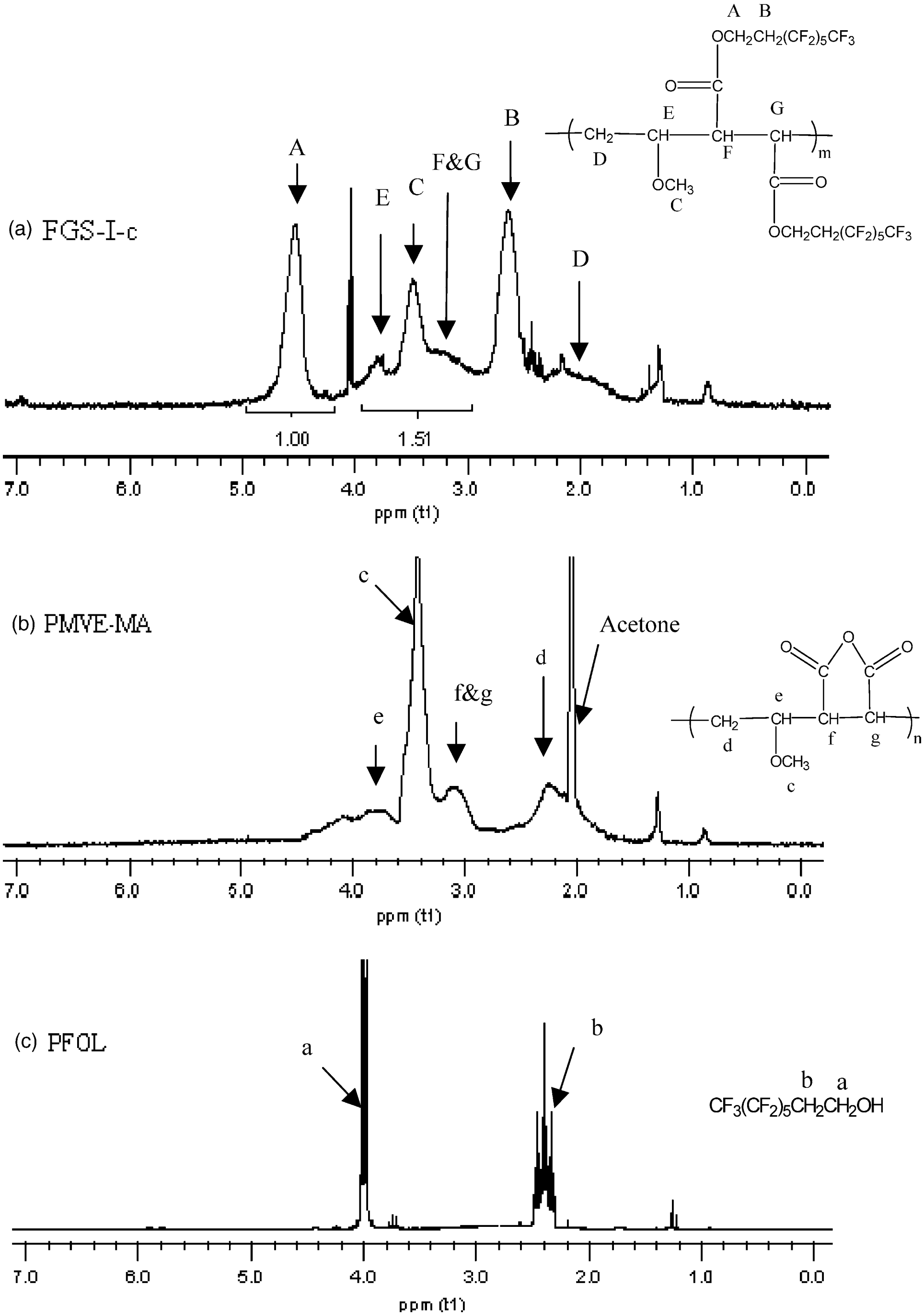


Fig. 3. $^1$H NMR spectra (a) FGS-I-c; (b) PMVE-MA; (c) PFOL. Note that the graft degree was determined from the integration peak A (two protons) and peaks E, C, F, G (six protons).

pans, which were heated up to 220 °C at a rate of 10 °C/min from room temperature (first heating cycle). After 5 min isothermal process, samples were cooled down to −50 °C at the same rate (cooling cycle); and then following another 5 min isothermal process, samples were heated up to 220 °C at 10 °C/min again (second heating cycle). Polymer surface areas were measured using the Brunauer–Emmett–Teller (BET) method with a Micromeritics ASAP 2020 nitrogen adsorption analyzer. The samples were outgassed overnight at the room temperature under vacuum before analysis.

## 3. Results and discussion

### 3.1. Synthesis and characterisation of stabilisers

F-*g*-PMVE-MA with a graft degree of 1.99 (i.e., FGS-I-c) was synthesised and tested in the polymerisation of VDF in $scCO_2$ in our previous work [25]. We found that F-*g*-PMVE-MA acted effectively as a stabiliser, leading to a high molecular weight PVDF product with well-defined polymer particles [25]. To further investigate the effect of the stabiliser architecture, a series of graft stabilisers were prepared by the same thermal ring opening esterification (Fig. 1) under reaction conditions listed in Table 1. Controlled by changing the mole ratios of A:B and the reaction time, FGS-I stabilisers with lower degrees of grafting (1.3 for FGS-I-a and 1.8 for FGS-I-b) were produced. FGS-IV stabiliser with a longer fluorinated graft chain R was also prepared to investigate the effect of the length of fluorinated graft chain. FGS-III with the side chain R′ of the backbone as alkyl rather than alkoxy was prepared to investigate the effect of the pendant group. FGS-II with a much longer polymer backbone was also prepared by the use of a high molecular weight PMVE-MA ($M_n = 1130$ kg/mol) as the starting material. NFGS is non-fluorinated graft PMVE-MA copolymer (Fig. 2).

To determine the degree of grafting in the stabilisers, the $^1$H NMR spectra for both the starting material PFOL and the ring-opened stabiliser products (FGS-I, FGS-II and FGS-III) were obtained in an octafluorotoluene/$CDCl_3$ (50/50, v/v) mixture. The $^1$H NMR spectrum for the starting material PMVE-MA was obtained in deuterated acetone. The $^1$H NMR spectrum for NGFS was obtained in $CDCl_3$. A suitable deuterated solvent for FGS-IV was not found. However, FGS-IV was estimated to have a lower degree of grafting than FGS-I-c because during synthesis a portion of the fluorinated alcohol PFDL solidified in the upper part of the condenser due to its high melting point (95 °C), leading to a mole ratio of PMVE-MA and PFDL much higher than the theoretical value (1.0:4.0).

The $^1$H NMR spectrum of PMVE-MA (Fig. 3(b)) shows signals at 3.3–2.9 ppm for the $CH$ (f,g) in the ring, 4.5–3.6 ppm for the $CH$ (e) linked to $OCH_3$ in the backbone and 2.6–1.7 ppm for $CH_2$ (d) in the backbone. There is also a strong $CH_3$ (c) indicated at 3.35 ppm. After thermal ring-opening, there are two strong signals at 4.5 and 2.6 ppm for the $OCH_2$ (**A**) and $CH_2CF_2$ (**B**) in the fluorinated graft chains (Fig. 3(a)). Comparing with $^1$H NMR spectrum of the starting fluorinated alcohol (Fig. 3(c)), these two signals have shifted from 4.0 (a) and 2.4 (b) ppm respectively, where a residue of the alcohol leaves weak signals at these two positions.

The degree of grafting is an important issue in the synthesis of these stabilisers. In each case, this can be estimated from $^1$H NMR. For FGS-I-c, the integration of the peak **A** at 4.5 ppm for the $OCH_2$ in the fluorinated graft chains is 100 (two protons). The total integration of peaks in the range of 4.0–3.0 ppm for $CH$ (**F** and **G**, two protons) in the ring, $CH$ (**E**, one proton) linked to $OCH_3$ in the backbone and $CH_3$ (**C**, three protons) is 151 (a total of six protons). Therefore, the graft degree of FGS-I-c is

$$\text{Graft Degree} = \frac{100/2}{151/6} = 1.99$$

The molecular weight of FGS-I-c was estimated as ca. 400 kg/mol, based on the $M_n$ of PMVE-MA (79.8 kg/mol) and the graft degree (1.99). By this method, the degrees of grafting for FGS-I-a, FGS-I-b and FGS-II were also obtained (Table 1).

The degree of grafting for FGS-III (1.3) was determined by using the integration peak A (30 protons) and peak B (two protons) in the $^1$H NMR spectrum (Fig. 4). This indicates that PMA-OD has a lower reactivity than PMVE-MA towards esterification with PFOL.

The degree of grafting for NFGS (1.6) was determined from the integration peak A (three protons) and peak B (three protons) in the $^1$H NMR spectrum (Fig. 5).

$^{19}$F NMR analysis (Fig. 6) was also performed for FGS-I-c and PFOL in the mixture of $CDCl_3$ and octafluorotoluene (50/50, v/v). Typical broader peaks for FGS-I-c copolymer were observed. However, the degree of grafting cannot be obtained from $^{19}$F NMR spectrum because there are no other characteristic fluorine atoms in the product apart from those in the fluorinated graft chains.

If there is a partially grafted one-arm structure, carboxylic acid end groups should exist in the polymer chain. $^{13}$C NMR analysis (Fig. 8) was performed for the product FGS-I-c to detect the presence of carboxylic acid groups in the polymer chain. Comparison with the $^{13}$C NMR spectra of succinic acid

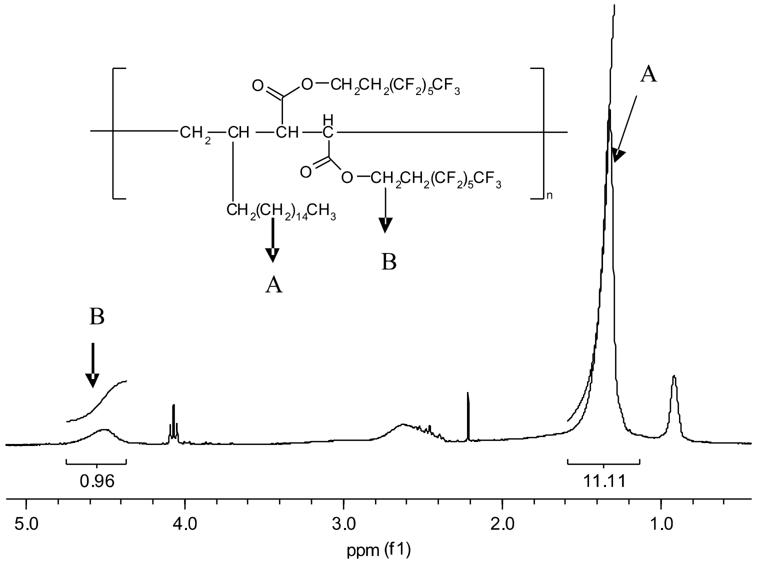


Fig. 4. $^1$H NMR spectrum of FGS-III. Note that the degree of grafting (1.3) was determined from the integration peak A (30 protons) and peak B (two protons).

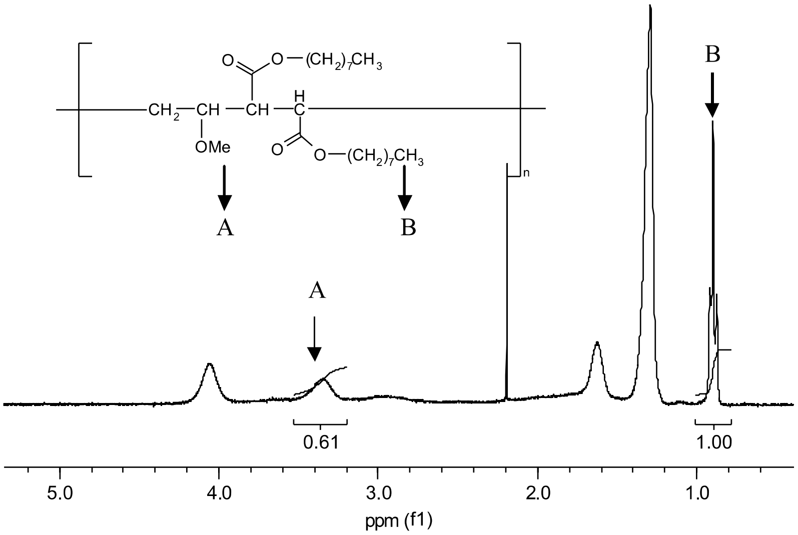


Fig. 5. $^{1}$H NMR spectrum of NFGS. Note that the degree of grafting (1.6) was determined from the integration peak A (three protons) and peak B (three protons).

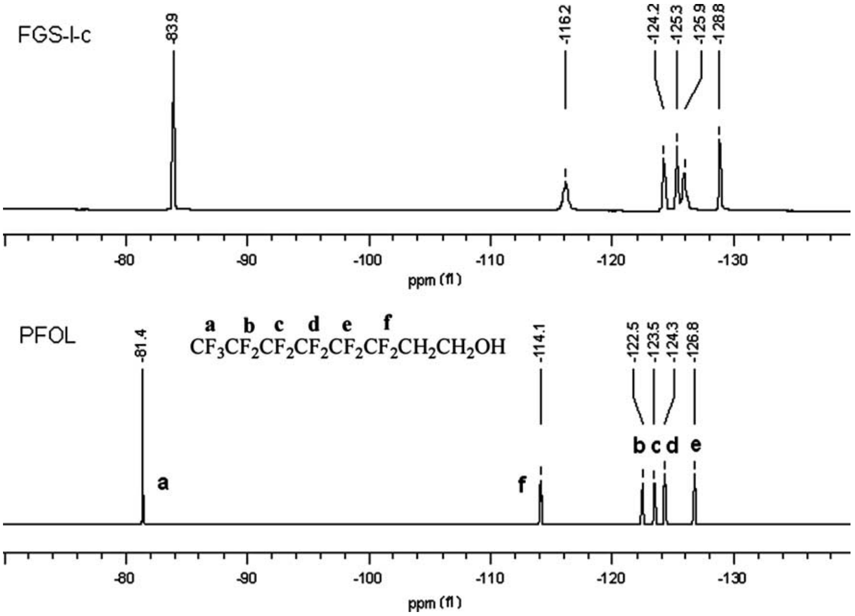
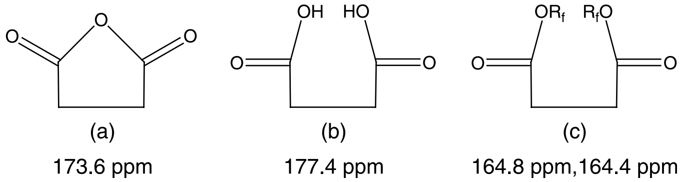


Fig. 6. $^{19}$F NMR spectra (a) FGS-I c; (b) PFOL. Note that typical broader peaks for FGS-I-c copolymer were observed because the fluorinated chains were incorporated with PMVE-MA copolymers.

(in $D_2O$), succinic anhydride (in deuterated acetone), and succinic anhydride ester (in a mixture of $CDCl_3$ and octafluorotoluene (50/50, v/v)), which have similar molecular structures as PMVE-MA, PMVE-MA acid and PMVE-MA ester, were made. Chemical shifts were obtained for succinic acid (177.4 ppm), succinic anhydride (173.6 ppm), and succinic anhydride ester (164.8 and 164.4 ppm). These results indicate that anhydrides have a lower chemical shift than acid, and ester has lower chemical shift than anhydride (Fig. 7). $^{13}$C NMR spectra (Fig. 8) for FGS-I-c, starting material PMVE-MA, and the hydrolysis product of PMVE-MA corresponded well with this pattern. The spectrum for FGS-I-c ((b) in Fig. 8) did not show obvious characteristic peaks at 175 and 177 ppm for the carboxylic acid group. However, the spectrum for FGS-I-a ((a) in Fig. 8), with a lower degree of grafting (1.3), showed some differences of the intensities of peaks from the stabiliser (FGS-I-c) with a high degree of grafting (2.0), and indicated the shoulder for the carboxylic acid group.



(a) 173.6 ppm

(b) 177.4 ppm

(c) 164.8 ppm,164.4 ppm

Fig. 7. $^{13}$C NMR chemical shifts (a) succinic anhydride; (b) succinic acid; (c) succinic ester. Note that the order of chemical shifts from the smallest to the largest is ester, anhydride, and then acid.

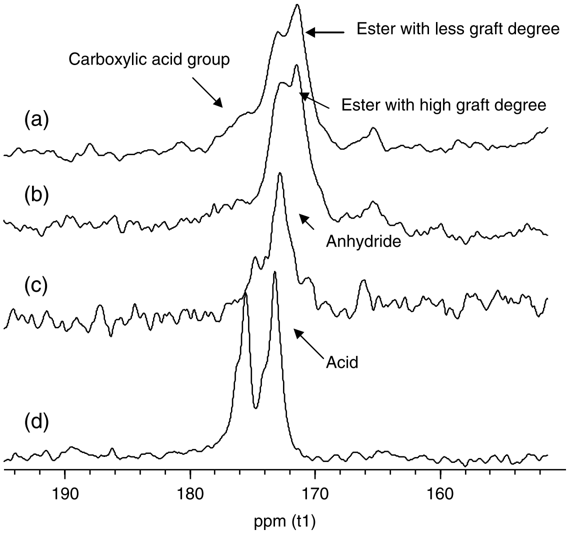


Fig. 8. $^{13}$C NMR spectra. (a) FGS-I-a (graft degree 1.3) (173.0, 171.5 ppm); (b) FGS-I-c (graft degree 2.0) (173.0, 171.5 ppm); (c) starting material PMVE-MA (175.4, 173.4 ppm); (d) PMVE-MA acid (177.6, 175.4 ppm); the hydrolysis product of PMVE-MA. Note that the order of chemical shifts for ester, anhydride and acid displays the same pattern as that in Fig. 7.

DRIFTS was used to obtain FTIR spectra from the solid samples of the starting material and the stabiliser products. PMVE-MA, FGS-I, FGS-II, and FGS-IV, were finely ground with potassium bromide (KBr) (approximately 3% sample in 97% KBr). The diffuse reflectance spectrum of PMVE-MA (Fig. 9) revealed three characteristic peaks in the carbonyl region [26] at 1800–1600 cm$^{-1}$. The band near 1850 cm$^{-1}$ can be assigned to be symmetric $(C{=}O)_2$ stretch, a strong band near 1785 cm$^{-1}$ can be assigned to be antisymmetric $(C{=}O)_2$ stretch. The band near 1730 cm$^{-1}$ can be assigned to be C=O stretch for carboxylic acid groups in the copolymer [29]. Following thermally activated nucleophilic ring opening in the presence of the fluorinated alcohol (PFOL or PFDL), the spectra (Fig. 9) of the products showed distinct peaks in the position of an ester (1738 cm$^{-1}$). The spectrum for FGS-I-c, with a high degree of grafting, showed one peak in the carbonyl region with a shoulder; in contrast, for FGS-I-a, with a lower degree of grafting, the spectrum still showed three peaks in the carbonyl region (Fig. 9). These data demonstrate that maleic anhydride units have undergone thermal ring-opening reaction with the fluorinated alcohols. The most characteristic feature in the spectra of fluorinated hydrocarbons are the strong C–F stretching modes occurring in the 1250–800 cm$^{-1}$ region [29].

The DSC trace for PMVE-MA (Fig. 10(a)) was modified after esterification. PMVE-MA is an amorphous copolymer, with a glass transition temperature ($T_g$) around −12.20 °C. The trace started to drift down at 60 °C indicating degradation (data confirmed by TGA). However, the DSC traces for FGS-I showed a melting peak ($T_m$) at about $63 \pm 5$ °C, indicating the introduction of crystallinity after esterification. In addition, TGA results indicated that the fluorinated graft stabilisers have better thermal stability than the starting materials PMVE-MA and PMA-OD due to the incorporated fluorinated chains.

### 3.2. Phase behaviour of stabilisers in scCO$_2$, VDF and mixture of scCO$_2$ and VDF

The phase behaviour studies (Fig. 11) showed that a high degree of grafting increases solubility in scCO$_2$. For a fluoropolymer having a hydrocarbon backbone and a fluorocarbon pendant group, CO$_2$ solubility depends on both the number of fluorinated side groups and the molar mass of the side groups relative to the hydrocarbon main chain [13].

FGS-IV (with longer fluorinated graft chain length, but low degree of grafting) showed similar solubility to FGS-I-c (Fig. 12). According to the results demonstrated in Fig. 11,

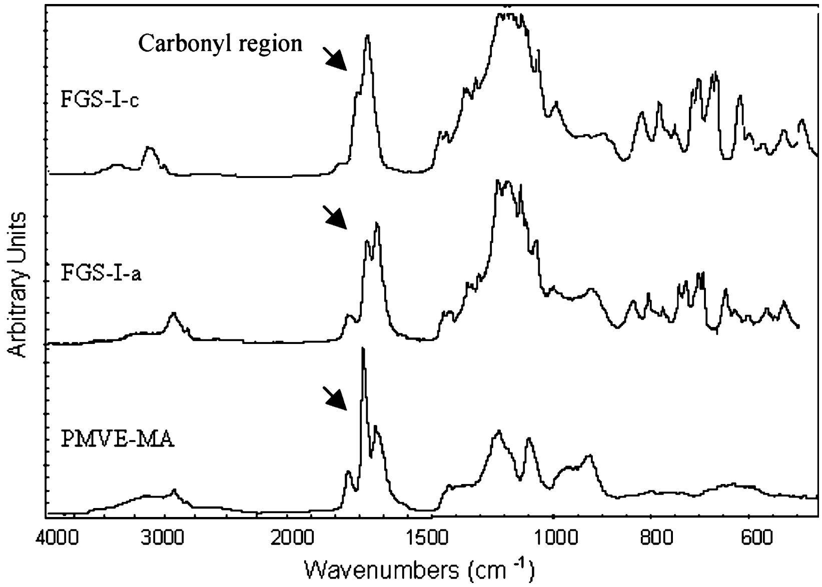


Fig. 9. Diffuse reflectance spectra of PMVE-MA, FGS-I-a and FGS-I-c. Note that the carbonyl region showed a distinct peak in the position of ester (1738 cm$^{-1}$). A high degree of grafting (FGS-I-c) leads to distinct changes in the carbonyl region, demonstrating the removal of maleic anhydride units.

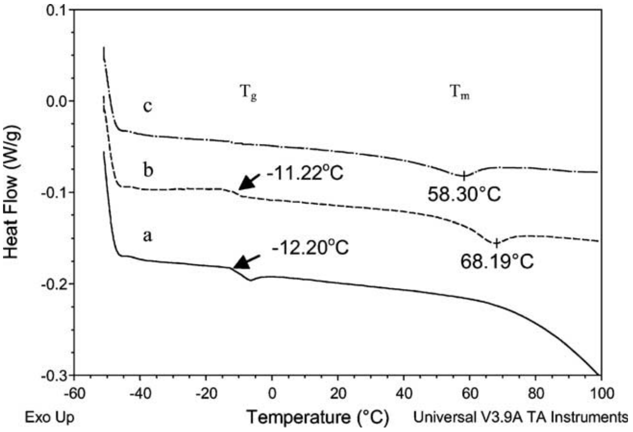


Fig. 10. DSC traces (a) PMVE-MA; (b) FGS-I-a); (c) FGS-I-c. Note that the esterification introduces crystallinity ($T_m$) and high degree of grafting leads to the change of the glass transition temperature ($T_g$).

the degree of grafting has a significant impact on the solubility of stabiliser. The reason for FGS-IV having a similar solubility to FGS-I-c even with a relatively low degree of grafting, is that its long fluorinated graft chain makes a good contribution to its solubility. Moreover, Fig. 12 demonstrates that the stabiliser with longer polymer backbones (FGS-II) has a slightly lower solubility than that with shorter polymer backbones (FGS-I-c). As one might expect, the stabiliser with an alkyl pendant group (FGS-III) has a much lower solubility than the stabiliser with an alkoxy pendant group (FGS-I-c). In addition, the non-fluorinated stabiliser (NFGS) was only partially soluble in $scCO_2$ at a concentration of 1.2 wt% with respect to $CO_2$ even at the maximum working pressure (6000 psi (40.82 MPa)) of the view cell.

For comparison, the solubility of the stabilisers in pure VDF was also studied (Fig. 13), demonstrating that VDF is a better solvent than $CO_2$ for these fluorinated stabilisers.

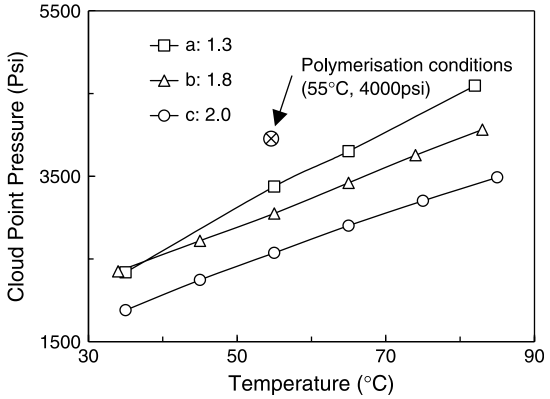


Fig. 11. Cloud point curves for the fluorinated graft stabilisers with different degrees of grafting in pure $CO_2$. (a) FGS-I-a, 1.3; (b) FGS-I-b, 1.8; (c) FGS-I-c, 2.0. The concentration of stabilisers = 1.2 wt% wrt $CO_2$ employed. Note that a high degree of grafting increases the solubility in $scCO_2$. The lines are below polymerisation conditions, indicating stabilisers are soluble in $scCO_2$.

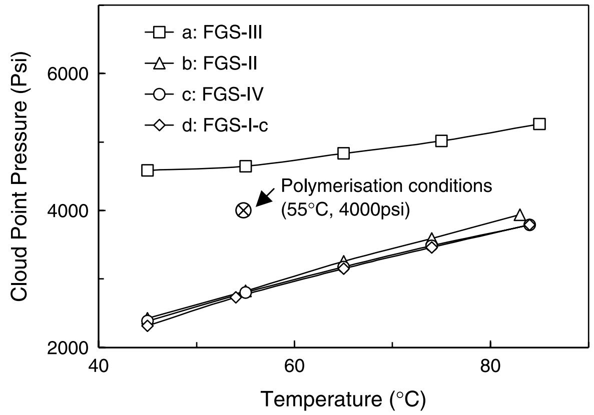


Fig. 12. Cloud point curves for the fluorinated graft stabilisers in pure $CO_2$: effect of the architecture (a) FGS-III; (b) FGS-II; (c) FGS-IV; (d) FGS-I-c. The concentration of stabilisers = 1.2 wt% wrt $CO_2$ employed. Note that the stabiliser with an alkyl pendant group (FGS-III) has a much lower solubility than the others.

### 3.3. Polymerisations of VDF in $scCO_2$ in presence of graft stabilisers: effect of architecture on molecular weight and morphology of the PVDF polymers

F-*g*-PMVE-MA with graft degree as 1.99 (i.e., FGS-I-c) was found to act as an effective stabiliser for the polymerisation of VDF in $scCO_2$, leading to a high molecular weight PVDF product with well-defined polymer particles [25]. FGS-I-a, FGS-II, FGS-III, FGS-IV and NFGS were all tested under the same polymerisation conditions (Table 2). The results (Table 2) showed that the stabiliser architecture had no significant impact on the molecular weight and molecular weight distribution of PVDF products.

The dispersion polymerisations with the fluorinated graft stabilisers (FGS-I to FGS-IV) all lead to high molecular weight products ($M_w = 300–350$ kg/mol), and the PVDF products (PVDF-1 to PVDF-5 in Table 2) obtained are in the form of fine powders. However, the morphologies of the PVDF polymers observed by SEM indicated some differences.

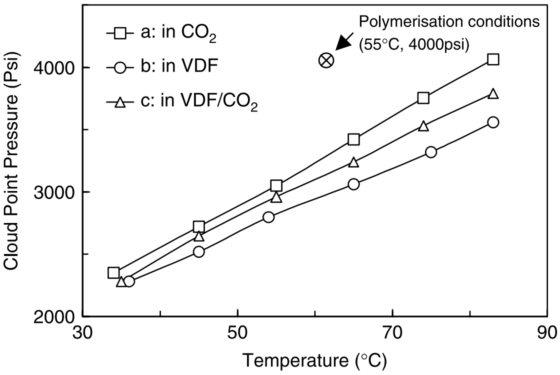


Fig. 13. Cloud point curves for FGS-I-c in (a) pure $CO_2$; (b) pure VDF; (c) a mixture of VDF and $CO_2$ (50/50, w/w). The concentration of the stabiliser = 1.2 wt% wrt the media employed ($CO_2$, VDF, or VDF/$CO_2$). Note that VDF is a better solvent than $CO_2$ for these fluorinated stabilisers.

Table 2
Experimental data for the polymerisations of VDF using the graft stabilisers

| Entry | PVDF sample | Stabiliser employed | $R_p$[a] (g/min l) | GPC result of PVDF polymers | | Morphology of PVDF polymers | |
|---|---|---|---|---|---|---|---|
| | | | | $M_w$[b] | PDI[c] | Appearance[d] | SEM images[e] |
| 1 | PVDF-1 | FGS-I-a | 0.20 | 343 | 2.5 | Fine powder | (a) in Fig. 14 |
| 2 | PVDF-2 | FGS-I-c | 0.35 | 338 | 3.6 | Fine powder | (b) in Fig. 14 |
| 3 | PVDF-3 | FGS-II | 0.23 | 335 | 2.7 | Fine powder | – |
| 4 | PVDF-4 | FGS-III | 0.33 | 339 | 2.7 | Fine powder | – |
| 5 | PVDF-5 | FGS-IV | 0.25 | 305 | 2.5 | Fine powder | – |
| 6 | PVDF-6 | NFGS | 0.67 | 551 | 3.4 | Spongy solid | (b) in Fig. 15 |
| 7 | PVDF-7 | PFOL | 0.86 | 646 | 3.4 | Spongy solid | (c) in Fig. 15 |
| 8 | PVDF-8 | – | 0.33 | 216 | 2.3 | Spongy solid | (d) in Fig. 15 |

Reactions were carried out at 55 °C, an initial vessel pressure $P_0 = 4000$ psi (27.21 MPa), concentration of VDF monomer [M] = 9.8 mol/l, concentration of initiator [I] = 1.5 mmol/l, stirring rate = 100 rpm; concentration of stabiliser [S] = 0.52 wt% weight/weight relative to VDF monomer, monomer conversion less than 5%, solid contents in the autoclave = ~33 g/l.

[a] Polymerisation rate, defined as the average weight of polymer produced per minute in 1 l vessel.

[b] Weight average molecular weight.

[c] Polydispersity.

[d] Determined by visual observation.

[e] Determined by SEM analysis.

### 3.4. Effect of degree of grafting: FGS-I-a and FGS-I-c

The fluorinated graft stabiliser having a higher degree of grafting (FGS-I-c) is a better stabiliser for the polymerisation of VDF in $scCO_2$ than the one having a lower degree of grafting (FGS-I-a) because more well-defined and discrete particles obtained (Fig. 14(b)). A high degree of grafting provided the macromolecular chains with larger free volumes, which led to the stronger steric stabilisation for the PVDF particles.

### 3.5. Effect of chain length of polymer backbone: FGS-II and FGS-I-c

The use of the fluorinated graft stabiliser with longer polymer backbones (FGS-II) produced the PVDF polymer particles qualitatively appearing to be smaller in diameters and more discrete. This is because the longer molecular chains can act more effectively to protect the PVDF primary particles from tangling and aggregating together.

### 3.6. Effect of pendant side groups: FGS-III and FGS-I-c

Phase behaviour study (Fig. 12) demonstrated that 1.2 wt% FGS-III in pure $CO_2$ was not totally soluble under the polymerisation conditions (55 °C and 4000 psi). However, visual observation by view cell demonstrated that 0.52 wt% of FGS-III in the mixture of $VDF/CO_2$ under the polymerisation conditions stated in Table 2 was totally dissolved. The polymerisation also started as a single phase, which is the case for other fluorinated stabilisers. The SEM images for the PVDF polymer product demonstrated that some fibre-like and aggregated solid were mixed with the polymer particles after the use of FGS-III (similar to (a) in Fig. 14). It is likely that the low molecular weight ($M_n$ of starting backbone PMA-OD = 30–50 kg/mol) and the low degree of grafting (1.3) of FGS-III, along with the alkyl pendant group, all combine to produce a low stabilisation activity.

### 3.7. Effect of fluorinated graft chain length: FGS-IV and FGS-I-c

SEM results demonstrated that the use of the fluorinated graft stabiliser with longer fluorinated graft chain length (FGS-

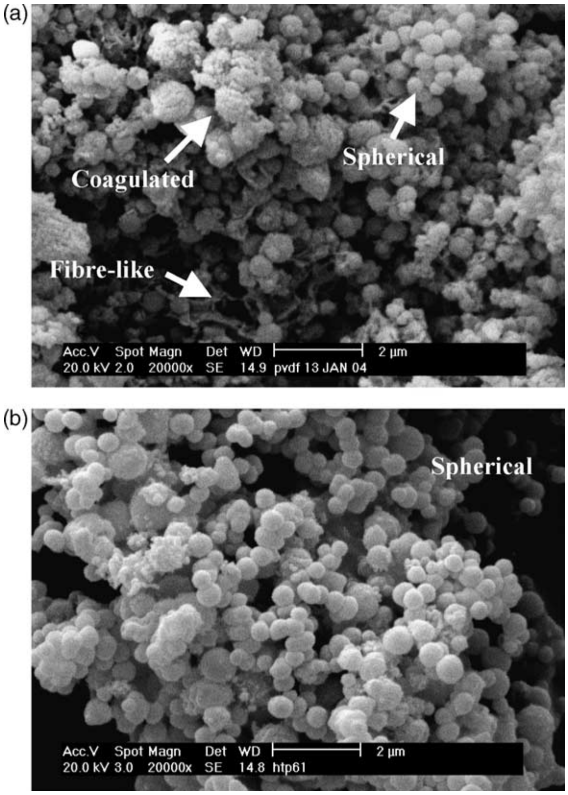


Fig. 14. Effect of the degree of grafting of the morphology of the PVDF polymers produced in $scCO_2$. (a) PVDF-1, in the presence of FGS-I-a (the degree of grafting = 1.3); (b) PVDF-2, in the presence of FGS-I-c (the degree of grafting = 2.0. The stabiliser with a higher degree of grafting (FGS-I-c) leads to a better stabilisation effect for the polymerisation of VDF as evidenced by the improved morphology of the polymer particles (b).

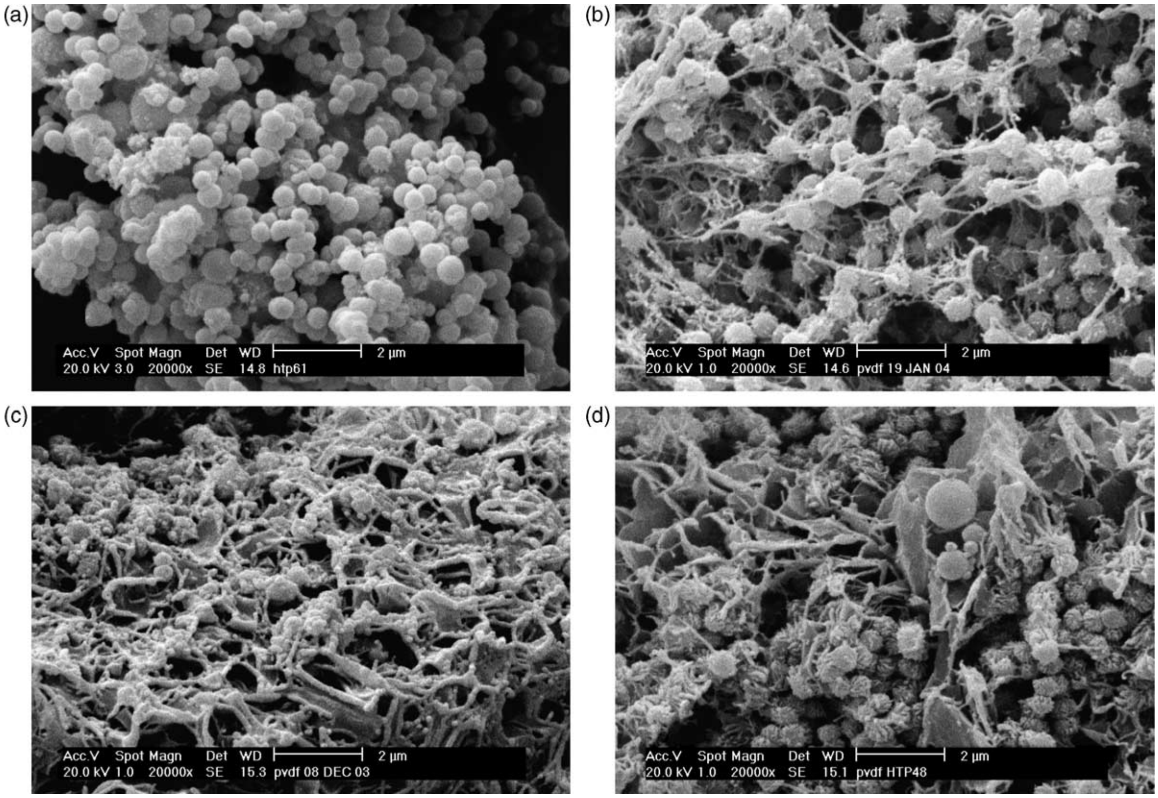


Fig. 15. Comparison of the morphologies of PVDF polymers produced in $scCO_2$ (a) PVDF-2, in the presence of FGS-I-c; (b) PVDF-6, in the presence of NFGS; (c) PVDF-7, in the presence of PFOL; (d) PVDF-8, in the absence of stabilisers.

IV) also led to well-defined PVDF polymer particles, despite its low degree of grafting. This indicated that the longer fluorinated graft chain played a role in this stabilisation.

In summary, all the fluorinated graft stabilisers synthesised in this work, including FGS-I-a, FGS-I-c, FGS-II, FGS-III and FGS-IV, led to well-defined polymer particles with high molecular weights. Some fine adjustment of the morphology of PVDF polymers can be achieved by changing the architecture of the molecular structure.

### *3.8. Effect of non-fluorinated graft stabiliser: NFGS*

Using the non-fluorinated graft stabiliser (NFGS) led to very high molecular weight spongy solid product (entry 6 in Table 2) of 551 kg/mol. Analysis by SEM ((b) in Fig. 15) showed spherical but aggregated polymer particles. By contrast, in the absence of any stabiliser ((d) in Fig. 15), only fibre- and sheet-like materials with a few particles are obtained. Thus it is clear that NFGS acted as a weak stabiliser for the polymerisation of VDF in $scCO_2$. The phase behaviour study demonstrated that part of NFGS was soluble in $scCO_2$. It is likely the soluble portion of NFGS worked somehow as the stabiliser for this polymerisation system.

### *3.9. Effect of fluorinated alcohol: PFOL*

A small amount of residue fluorinated alcohol PFOL was detected by $^1H$ NMR in the stabilisers. In order to determine whether this played a role in the stabilisation of the polymer particles during the polymerisation of VDF, PFOL was tested as a stabiliser under the same polymerisation conditions (entry 7 in Table 2). The product (PVDF-7) had a very high molecular weight (646 kg/mol). However, it is not fine powder but a spongy solid. Its SEM image ((c) in Fig. 15) showed sheet-like and fibre-like monoliths, indicating that PFOL cannot stabilise PVDF particles.

SEM data indicated that neither NFGS nor PFOL acted as effective stabilisers. We speculate that the high molecular weight products synthesised (PVDF samples 6 and 7) are most likely due to the polymerisations occurring within coagulated polymer phases.

The morphology for PVDF-8, observed by SEM, is fibre-like spongy structure ((d) in Fig. 15), by contrast, PVDF-2 shows well defined particles ((a) in Fig. 15). Surface area analysis (Table 3), measured by $N_2$ adsorption/desorption using the BET method, also showed a difference between these two samples. PVDF-8 has a surface area and pore volume ten

Table 3
The results from surface area analysis

| Results | PVDF-2 | PVDF-8 |
|---|---|---|
| BET surface area ($m^2/g$) | 3.20 | 40.08 |
| Langmuir surface area ($m^2/g$) | 5.00 | 58.92 |
| *t*-Polt external surface area ($m^2/g$) | 3.94 | 40.84 |
| Pore volume ($<180$ nm) ($cm^3/g$) | 0.012 | 0.168 |
| Pore size, adsoption average pore width (Å) | 143.87 | 167.44 |

Table 4
DSC results

| No | Stabiliser empo-lyed | $T_m$ (°C) | $T_c$ (°C) | Crystallinity determined by melting enthalpy (%)[a] |
|---|---|---|---|---|
| PVDF-1 | FGS-I-a | 174.9 | 137.0 | 46.0 |
| PVDF-2 | FGS-I-c | 173.7 | 131.0 | 39.0 |
| PVDF-3 | FGS-II | 172.0 | 135.8 | 42.6 |
| PVDF-4 | FGS-III | 172.6 | 137.0 | 44.4 |
| PVDF-5 | FGS-IV | 172.6 | 133.3 | 40.7 |
| PVDF-6 | NFGS | 177.5 | 141.6 | 57.8 |
| PVDF-7 | PFOL | 173.9 | 137.4 | 62.1 |
| PVDF-8 | – | 173.0 | 128.8 | 53.0 |

[a] Standard heat of fusion used for calculation is 104.5 J/g, i.e., the melting enthalpy ($\Delta H_0$) of totally crystalline material.

times larger than that of PVDF-2. These results reflect the porous structure of PVDF-8.

A crystallisation process during polymerisation might play a role in the significantly different morphologies of PVDF polymers. To gain further understanding, DSC analysis was performed to determine the degree of crystallinity ($\Phi_{DSC}$) for PVDF polymers by:

$$\Phi_{DSC} = \Delta H_m / \Delta H_0$$

where $\Delta H_m$ is the melting enthalpy of the material under study and $\Delta H_0$ is the melting enthalpy of 100% crystalline material ($\Delta H_0 = 104.50$ J/g for PVDF) [30]. The results (Table 4) show that the use of the fluorinated graft stabilisers decreases the degree of crystallinity of the PVDF polymers from 53 to less than 46%, and increases their crystallisation temperatures (131–137 °C). However, it has no significant influence on the melting temperature (172–177 °C) of the polymers. By contrast, the degrees of crystallinity for the PVDF polymers obtained in the presence of NGFS and PFOL increased, compared to those for the polymers produced without any stabilisers. DSC results imply that materials with a low degree of crystallinity were more likely to have better morphology than those with a high degree of crystallinity.

## 4. Conclusions

A group of graft stabilisers both fluorinated and non-fluorinated were synthesised and characterised in detail. High molecular weight PVDF polymer products with well-defined and uniform spherical particles (diameter at 200–500 nm) have been obtained by the polymerisations of VDF in $scCO_2$ using these fluorinated graft copolymer stabilisers. The effect of the architecture of the stabilisers, including the addition of fluorinated graft chains with different chain lengths, varying the degree of graft chain incorporation, and the use of a longer polymer backbone are reported in detail. The fluorinated graft stabiliser with a high degree of grafting, high molecular weight, and an alkoxy pendant group is the most effective stabiliser for the polymerisation of VDF in $scCO_2$.

## Acknowledgements

We gratefully acknowledge the European Community for funding (ECOPOL project number: GRD1-2001-40294). We thank Dr Y. Xia for BET analysis. We thank also Dr D. Bratton, Dr C.J. Duxbury and Mr A. Naylor for their advice; Mr R.G.M. Wilson, Mr P.A. Fields and Mr M.P. Dellar for their technical support. SMH is a Royal Society Wolfson Research Merit Award holder.

## References

[1] Leitner W. Acc Chem Res 2002;35(9):746–56.
[2] Woods HM, Silva MMCG, Nouvel C, Shakesheff KM, Howdle SM. J Mater Chem 2004;14(11):1663–78.
[3] Kendall JL, Canelas DA, Young JL, DeSimone JM. Chem Rev 1999; 99(2):543–63.
[4] DeSimone JM, Maury EE, Menceloglu YZ, McClain JB, Romack TJ, Combes JR. Science 1994;265(5170):356–9.
[5] Hsiao YL, Maury EE, DeSimone JM, Mawson S, Johnston KP. Macromolecules 1995;28(24):8159–66.
[6] O'Neill ML, Yates MZ, Johnston KP, Smith CD, Wilkinson SP. Macromolecules 1998;31(9):2838–47.
[7] Shaffer KA, Jones TA, Canelas DA, DeSimone JM, Wilkinson SP. Macromolecules 1996;29(7):2704–6.
[8] Wang W, Griffiths RMT, Naylor A, Giles MR, Irvine DJ, Howdle SM. Polymer 2002;43(25):6653–9.
[9] Lepilleur C, Beckman EJ. Macromolecules 1997;30(4):745–56.
[10] Giles MR, Griffiths RMT, Aguiar-Ricardo A, Silva MMCG, Howdle SM. Macromolecules 2001;34(1):20–5.
[11] DeSimone JM, Riddick L. Proceedings—NOBCChE 1999;26:53–61.
[12] Sarbu T, Styranec T, Beckman EJ. Nature 2000;405(6783):165–8.
[13] Baradie B, Shoichet MS. Macromolecules 2002;35(9):3569–75.
[14] Klinge U, Klosterhalfen B, Ottinger AP, Junge K, Schumpelick V. Biomaterials 2002;23(16):3487–93.
[15] Howe-Grant M. Fluorine chemistry: a comprehensive treatment. New York: Wiley; 1995.
[16] Ameduri B, Boutevin B, Kostov GK, Petrova P. Des Monomers Polym 1999;2(4):267–85.
[17] McCarthy TF, Williams R, Bitay JF, Zero K, Yang MS, Mares F. J Appl Polym Sci 1998;70(11):2211–25.
[18] Apostolo M, Albano M, Storti G, Morbidelli M. Macromol Symp 2000; 150:65–71.
[19] Ameduri B, Boutevin B. J Fluorine Chem 2000;104(1):53–62.
[20] Barber LA. Barber LABarber LAs; (Pennwalt Corp., USA). EP patent 169328; 1986.
[21] Charpentier PA, Kennedy KA, DeSimone JM, Roberts GW. Macromolecules 1999;32(18):5973–5.
[22] Charpentier PA, DeSimone JM, Roberts GW. Ind Eng Chem Res 2000; 39(12):4588–96.
[23] Saraf MK, Gerard S, Wojcinski LM, Charpentier PA, DeSimone JM, Roberts GW. Macromolecules 2002;35(21):7976–85.
[24] Tai H, Wang W, Martin R, Liu J, Lester E, Licence P, et al. Macromolecules 2005;38(2):355–63.
[25] Tai H, Wang W, Howdle SM. Macromolecules 2005;38(5):1542–5.
[26] Giles MR, O'Connor SJ, Hay JN, Winder RJ, Howdle SM. Macromolecules 2000;33(6):1996–9.
[27] Licence P, Dellar MP, Wilson RGM, Fields PA, Litchfield D, Woods HM, et al. Rev Sci Instrum 2004;75(10):3233–6.
[28] Strain F, Bissinger WE, Dial WR, Rudolf H, DeWitt BJ, Stevens HC, et al. J Am Chem Soc 1950;72:1254–63.
[29] Sadtler Research Laboratories. The infrared spectra atlas of monomers and polymers. Philadelphia: Sadtler Research Laboratories; 1980.
[30] Lanceros-Mendez S, Mano JF, Costa AM, Schmidt VH. J Macromol Sci-Phys 2001;B40(3–4):517–27.