

Multi-End Functionalised Polymer Additives Synthesised by Living Anionic Polymerisation – the Impact of Additive Molecular Structure upon Surface Properties.

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Abstract Numerous applications require specific properties at polymer surfaces that differ from the bulk. Herein we describe the novel synthesis of a series of multi-end functionalised poly(styrene) and poly(isoprene) additives carrying 1 to 3 fluoroalkyl (CF) groups. The additives were prepared by end capping the living chain ends of polymers prepared via living anionic polymerisation. The resulting polymers have been used as additives to render the surface of polymer films hydrophobic/lipophobic and we have characterised these polymer films using static contact angle measurements with water as the contact fluid. We have found that additive molecular weight, the number of CF groups, additive concentration and annealing conditions have a significant impact upon the resulting surface properties. Increasing the additive concentration and/or number of CF groups resulted in higher contact angles whereas increasing the molecular weight of additive reduced contact angles and surface hydrophobicity. It has been discovered that these additives undergo rapid adsorption to the surface of a thin film in the time taken to produce the film by spin coating and the result is significantly enhanced surface properties. Annealing polystyrene films above the glass transition temperature revealed some interesting behaviour in so much that it demonstrated that on many occasions it is preferable to anneal films containing very small quantities of additive rather than to simply add greater quantities of additive. In addition to contact angles measurements, Rutherford backscattering analysis (RBS) has been carried out on examples of modified poly(isoprene) films to quantitatively analyse the effect of additive molecular weight and number of fluoroalkyl groups on the near surface elemental composition of the modified thin films and confirming the relationship (described above) between these additive molecular parameters and surface adsorption. Finally, we have described a model which compares the behaviour of the additives in thin films to surfactants in solution.

30 Introduction

There are frequent circumstances where it is desirable for the properties at the surface of a polymer to be distinctly different from the bulk properties. For example, surface chemistries which promote adhesion, wettability, biocompatibility, chemical resistance and hydrophobicity are attractive for a variety of applications. Low surface energy, highly fluorinated polymer surfaces are particularly appealing in terms of their liquid repellence, chemical inertness and low coefficient of friction and imparting these attributes to a surface can result in the polymers finding use in applications such as anti-fouling finishes, biomedical devices, release coatings and filter media¹. The use of fluorinated polymers to deliver these desirable properties is often impractical given their expense and the difficulty in processing such polymers. Poly(tetrafluoroethylene) (PTFE) for example, has a very high melting point (330 °C) and its melt viscosity is such that it cannot easily be processed via melt extrusion or injection moulding. However, since in many cases only the surface layer of a product needs to possess these specific properties, a much more efficient approach involves the use of a relatively

cheap commodity polymer to provide the desirable, mechanical bulk properties and modification of the surface to introduce the desired surface properties. Examples of current methodologies for fluorinating polymer surfaces include plasma treatments,¹⁻⁴ wet chemical modification⁵⁻⁷ and the application of polymeric surface coatings.^{8,9} although all of these approaches tend to suffer from (at least one of) being expensive, restricted to batch processing, safety hazards or the generation of large volumes of solvent waste.

60 An attractive alternative is the use of fluorinated additives and fluorine containing polymers to create low surface energy properties, although fluorinated polymers themselves, such as PTFE, are highly incompatible with the majority of conventional commodity polymers, making them very difficult to blend. Surface adsorption of additives will be spontaneous if there is an accompanying reduction in the surface energy and it is therefore relatively straightforward to increase the hydrophobicity of polymer surfaces by the use of polymers functionalised with low surface energy fluorocarbon (CF) groups. This is an approach that has been demonstrated previously using fluorine containing polymers of varying structures and with varying degrees of success¹⁰⁻⁴⁵; the relative merits and limitations of many of these approaches

have been recently reviewed⁴⁶. Compatibility of any additive with the matrix (bulk) polymer is crucial. The use of fluorinated block copolymers²⁴ as an additive relies on the surface segregation of the block copolymers to the air-polymer interface and the kinetics of surface segregation comes into play; incompatibility of the fluorinated block (with the bulk) results in unavoidable self organisation of the block copolymers into large aggregates, which significantly retards surface segregation. Even prolonged annealing above the glass transition temperature is insufficient to allow diffusion of the block copolymers from the bulk to the surface to give uniform coverage. In contrast, it is feasible to rapidly transform surface properties by the incorporation of low molecular weight functionalised additive molecules. However, unless such additives are able to subsequently react with the base polymer, which is rarely the case with many commodity polymers that are chemically inert (poly(ethylene), poly(propylene), poly(ethylene terephthalate), the additives are prone to compromise the bulk physical properties and they may also be removed from the surface via evaporation, dissolution or wear; hence the long term durability of surface properties will be significantly compromised.

In light of these apparent constraints, an alternative and attractive strategy for modifying surface properties is the use of end functionalised polymer chains which preferentially/spontaneously adsorb to the surface. Hirao⁴²⁻⁴⁴ prepared polystyrene polymers by anionic polymerization end capped with up to 32 C₈F₁₇ groups by an iterative methodology that involved many reaction steps. When these end capped polymers in their pure state - not as additives - were cast into films, it was found that surface properties were (not surprisingly) strongly dependant on the number of CF groups. Furthermore, XPS and static contact angle measurements suggest surface saturation of end-functionalized polymer chains in most cases when the number of CF groups reaches between 8 and 16, Static contact angle measurements of these films when the surface is saturated with CF groups were between 110 and 115° with water and between 53 and 56° with dodecane. More recently we have devised a structure for an end functionalised polymer, with the aim of developing the optimal molecular parameters for efficient surface modification when the functionalised polymers are used as additives in low concentrations. The structure is extremely versatile and consists of two distinct components; a multifunctional head group carrying a predetermined yet low number of fluoroalkyl groups, to which is attached a pendant polymer chain. This pendant polymer chain is intended to play two roles, firstly to provide long term durability for the modified surface through chain entanglement with the bulk sub phase and secondly to compatibilise the highly fluorinated head group with the bulk phase. We have recently shown that spontaneous surface segregation of such additives (carrying up to 4 CF groups) to be a particularly effective approach for the surface functionalisation of polymer thin films when used in low concentration⁴⁷⁻⁵⁰. Moreover, PTFE like surfaces were achieved with as little as 0.1 wt % of a 5,000 gmol⁻¹ poly(styrene) additive carrying 3 C₈F₁₇ groups. We have

previously reported the synthesis and characterisation of poly(styrene) and poly(methyl methacrylate) additives synthesised by atom transfer radical polymerisation⁴⁹ and poly(lactide) synthesised by ring opening polymerisation⁴⁷. Whilst these successful studies provided insights into the relationship between molecular parameters such as the number of fluoroalkyl groups carried by the additive and surface properties, limited information was obtained pertaining to the impact of molecular weight of additive on surface segregation and surface properties – such polymerisation mechanisms do not usually permit a high degree of control over molecular weight beyond relatively low molecular weights. To overcome this limitation we sought to develop an entirely new methodology for the synthesis of analogous polymer additives by living anionic polymerisation – anionic polymerisation being a truly living polymerisation mechanism capable of exerting control over both molecular weight and polydispersity index for polymers with molecular weights even in excess of 1,000,000 gmol⁻¹. Such control over the polymerisation process has allowed us to carry out an exhaustive study into the influence (and limitation) of molecular weight (and number of CF groups) on surface segregation and surface properties with a view to optimising the molecular parameters of the additive molecules. We herein report the development of a synthetic method for the synthesis of poly(styrene) and poly(isoprene) additives via anionic polymerisation, with a variety of molecular weights (5,000 – 45,000 gmol⁻¹) and carrying 1 – 3 CF groups. Surface properties were primarily investigated using static contact angle measurements, although Rutherford backscattering analysis (RBS) was carried out on examples of modified poly(isoprene) films to quantitatively analyse the affect of additive molecular weight and number of fluoroalkyl groups on the near surface elemental composition of the modified thin films - confirming the relationship between these additive molecular parameters and surface adsorption. Finally, comprehensive annealing studies of films containing the poly(styrene) additives revealed some unexpected insight into the relative merits of using increased amounts of additive in a thin film and annealing films containing very small amounts of additive.

Experimental

Materials

Benzene (HPLC grade), toluene (HPLC grade), styrene (> 99%), isoprene (> 99%), hexane (HPLC grade), cyclohexane (HPLC grade) (all Aldrich) were purified, dried and degassed by repeated freeze-pump-thaw cycles over calcium hydride (Aldrich). *sec*-Butyllithium (1.4 M in cyclohexane), 3,5-*tert*-butyl-4-hydroxytoluene (BHT) (99%), 3,5-dihydroxybenzyl alcohol (99%), anhydrous K₂CO₃ (99.995%), 18-crown-6 (99%), CBr₄ (99%), PPh₃ (99%) (all Aldrich), 3-(perfluorooctyl)propanol and 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane (98%, Fluorochem) were used as received. Tetrahydrofuran (THF, Aldrich), was purified by repeated freeze-thaw-pump cycles over sodium wire (Aldrich) and benzophenone (Aldrich) until the solution

remained purple. Dichloromethane (DCM) was provided by an inhouse solvent purification service.

Measurements

¹H NMR analysis was carried out on a Varian VNMRS 700 5 MHz and Bruker Avance-400 MHz spectrometer using CDCl₃ as a solvent. Spectra were referenced to the trace of CHCl₃ (7.27 ppm) present in the CDCl₃. Molecular weights were determined using triple detection size exclusion chromatography (SEC) on a Viscotek 302 with refractive 10 index, viscosity and light scattering detectors, and 2 x 300mm PLgel 5µm mixed C columns. THF was used as the eluent with a flow rate of 1.0 ml per min and at a constant temperature of 35 °C. The detectors were calibrated with a single poly(styrene) standard (Polymer Labs) and values of 15 dn/dc (mlg⁻¹) of 0.185 and 0.144 were used for poly(styrene) and poly(isoprene) respectively. Elemental micro-analysis (C, H, N, Br and F) was carried out on an Exeter Analytical, Inc. CE-440 Elemental Analyser. Melting points were determined on an Electrothermal 9100 capillary melting point apparatus.

20 Surface analysis

Thin films were prepared by spin-coating onto clean silicon wafers using a Cammax PRS14E photoresist spinner to obtain films thicknesses of approximately 250 nm (measured by ellipsometry). Thin films comprised of blends of matrix 25 polymer – poly(styrene) (PS) or poly(isoprene) (PI) – containing various concentrations of surface modifying additives of different molecular weight and different number of fluoroalkyl groups. The polymer blends were prepared by co-dissolving the required polymers in toluene to give 5 % 30 w/v solutions. Films were either analysed as unannealed – dried overnight under vacuum at room temperature to ensure complete evaporation of excess solvent – or annealed under vacuum at 150°C for various annealing times. Static contact angles were measured at room temperature using a Ramé-Hart 35 goniometer model 100. Angles were measured for annealed and unannealed films using water as the contact fluid, and all data quoted is the average of at least three and in most cases six individual contact angle measurements. A full statistical analysis of all the contact angle data has been carried out and 40 the standard deviation for any individual data point varies from approximately 0.25 to 1.25 in a few extreme cases but in the majority of cases varies between 0.3 and 0.7 – thus, an error bar representing a typical standard deviation of 0.5 has been added to figure 4 for illustrative purposes.

45 Rutherford Backscattering Analysis.

The near-surface concentration of fluorocarbon was determined by Rutherford backscattering (RBS) analysis using an NEC 5SDH Pelletron accelerator. A 1.3 MeV ⁴He⁺ beam was brought onto the sample surface at 85 ° (i.e. 5 ° grazing 50 incidence). Backscattered ⁴He⁺ ions were detected at 170 ° to the incident beam. Data were summed over 3 measurements of 1µC ⁴He⁺ on different spots of the sample surface ensuring a quality of statistical results. This procedure has been previously shown to give reliable depth distribution data.^{47,51}

55 Synthesis of end capping agents

3,5-(Di-3-(perfluorooctyl)propyloxy)benzyl bromide (1)

1 was prepared in three steps according to the previously reported procedure⁴⁹. 3-(Perfluorooctyl)propanol was converted to 3-(perfluorooctyl)propyl bromide (PFOPB) using 60 carbon tetrabromide/triphenyl phosphine (CBr₄/PPh₃) in dry THF/DCM. PFOPB was then added to 3,5-dihydroxybenzyl alcohol in dry acetone, in the presence of potassium carbonate and 18-crown-6 to yield 3,5-(di-3-(perfluorooctyl)propyloxy) benzyl alcohol via a Williamson etherification reaction. 65 Reaction with (CBr₄/PPh₃) converted the benzyl alcohol functionality to benzyl bromide to yield 1. ¹H NMR (400 MHz, CDCl₃, δ, ppm) 2.10 (m, 4H, CH₂CH₂CH₂), 2.30 (m, 4H, CH₂CF₂), 4.02 (t, 4H, CH₂O), 4.41 (s, 2H, CH₂Br), 6.38 (t, 1H, ArH), 6.54 (d, 2H, ArH). Elemental analysis, 70 calculated for C₂₉H₁₇BrF₃₄O₂: C, 31.01; H, 1.53; Br, 7.11; F, 57.50. Found: C, 31.03; H, 1.50; Br, 6.97; F, 57.32.

3,4,5-(Tri-3-(perfluorooctyl)propyloxy)benzyl bromide (2)

2 was prepared in 4 steps according to previously reported 75 procedures⁴⁹. 3-(Perfluorooctyl)propanol was converted to 3-(perfluorooctyl)propyl bromide (PFOPB) using carbon tetrabromide/triphenyl phosphine (CBr₄/PPh₃) in dry THF/DCM. PFOPB was then added to methyl-3,4,5-trihydroxybenzoate in dry acetone, in the presence of 80 potassium carbonate and 18-crown-6 to yield methyl-3,4,5-(tri-3-(perfluorooctyl)propyloxy)benzoate. Reaction with a suspension of fresh lithium aluminium hydride in dry THF yielded the benzyl alcohol which in turn was treated with CBr₄/PPh₃ to yield 2. ¹H NMR (400MHz, CDCl₃, δ, ppm) 2.03 85 (m, 2H, CH₂CH₂CH₂), 2.15 (m, 4H, CH₂CH₂CH₂), 2.26-2.46 (m, 6H, CF₂CH₂), 4.01 (t, 2H, CH₂O), 4.09 (t, 4H, CH₂O), 4.44 (s, 2H, CH₂Br), 6.63 (s, 2H, ArH). Elemental analysis, calculated for C₄₀H₂₂BrF₅₁O₃: C, 30.04; H, 1.39; Br, 5.00; F, 60.58. Found: C, 29.91; H, 1.39; Br, 4.91 ; F, 54.15.

90 Synthesis of Polymer Additives

All polymerisations were carried out by living anionic polymerisation using standard high vacuum techniques.

Poly(styrene) additives with 1CF group (PS1CF)

A typical PS1CF additive was prepared thus: benzene (100 ml) and styrene (7.29 g, 0.07 mol) were distilled, under vacuum, into the reaction apparatus. For a target molecular weight of 5,000 gmol⁻¹, *s*-butyllithium (BuLi) (1.04 ml of 1.4M solution, 1.46 mmol) was added by injection via a rubber septum, resulting in the characteristic orange colour of 100 polystyryllithium. The solution was stirred at room temperature for at least an hour (longer for higher molecular weights), after which time the reaction was terminated by the injection of 1H,1H,2H,2H-perfluorodecyldimethyl chlorosilane (1.18 g, 2.19 mmol). The orange colour of the 105 living polymer solution dissipated instantly. The polymer was recovered by precipitation into methanol, collected by filtration, washed with further methanol and dried to constant mass in vacuo. Yield > 95%. M_n 5,700 gmol⁻¹, M_w 6,000 gmol⁻¹. ¹H NMR (700MHz, CDCl₃, δ, ppm): -0.1 – -0.3 (6H, 110 Si(CH₃), 5.90 – 7.70 (m, 5H, ArH). A further three PS1CF

additives were prepared by the same method – molecular weight analysis can be found in Table 1.

Poly(styrene) additives with 2CF groups (PS2CF)

A typical PS2CF additive was prepared thus: Toluene (50 ml) and styrene (2.94 g, 0.03 mol) were distilled, under vacuum, into the reaction apparatus. For a target molecular weight of 5,000 g mol^{-1} , *s*-BuLi (0.42 ml of 1.4M solution, 0.58 mmol) was injected via a rubber septum. The solution was stirred at room temperature for at least three hours (longer for higher molecular weights) before the addition of THF (25 ml) to the reaction flask by distillation, using a CO_2 /acetone bath to chill the receiving flask. Meanwhile, to a separate 25 ml round bottom flask fitted with a septum and sealed with a Young's tap, was added 3,5-(di-3-(perfluorooctyl)propyloxy)benzyl bromide (0.80 g, 0.71 mmol, 1.2 equiv w.r.t lithium) which was dried under high vacuum for several hours/overnight. The end capping agent was further purified azeotropically by the addition and subsequent removal (by distillation) of dry benzene. This process was repeated two more times and then the dried end capping agent was dissolved in 10 ml purified THF. The THF solution of the end capping agent was raised to atmospheric pressure with nitrogen gas, cooled in a CO_2 /acetone bath and then added by injection to the living polystyrene solution, at -78° Celsius, which resulted in the instant disappearance of the orange colour. The polymer was recovered by precipitation into an excess of methanol, collected by filtration, washed with further methanol and dried to constant mass in vacuo. Yield > 95%. M_n 4,900 g mol^{-1} , M_w 5,100 g mol^{-1} ; $^1\text{H NMR}$ (700MHz, CDCl_3 , δ , ppm): 3.75 – 3.88 (4H, $\text{ArOCH}_2\text{CH}_2$), 5.90 (m, 2H, *ArH*), 6.20 (m, 1H, *ArH*) and 6.25 – 7.30 (m, 5H, *ArH*). A further three PS2CF additives were prepared by the same method – molecular weight analysis can be found in Table 1.

Poly(styrene) additives with 3CF groups (PS3CF)

PS3CF additives were prepared in exactly the same fashion as that described above for PS2CF additives. Thus, toluene (50 ml) and styrene (3.00 g, 0.03 mol) were distilled, under vacuum, into the reaction apparatus. For a target molecular weight of 10,000 g mol^{-1} , *s*-BuLi (0.21 ml, 0.3 mmol) was injected via a rubber septum. The solution was stirred at room temperature for at least three hours (longer for higher molecular weights) before the addition of THF (25 ml) to the reaction flask by distillation using a CO_2 /acetone bath. Meanwhile, in a 25 ml round bottom flask (part of the same reactor and adjacent to the main reaction flask, 3,4,5-(tri-3-(perfluorooctyl)propyloxy)benzyl bromide (0.58 g, 0.36 mmol, 1.2 equiv w.r.t lithium), purified as described above, was dissolved in 10 ml purified THF. The THF solution of the end capping agent was then cooled in a CO_2 /acetone bath and then decanted into the living polystyrene solution, at -78° Celsius, which resulted in the instant disappearance of the orange colour. The polymer was recovered by precipitation into an excess of methanol, collected by filtration, washed with further methanol and dried to constant mass in vacuo. Yield > 95%. M_n 10,100 g mol^{-1} , M_w 10,400 g mol^{-1} ; $^1\text{H NMR}$ (700MHz, CDCl_3 , δ , ppm): 3.70 – 3.85 (4H, meta,

$\text{ArOCH}_2\text{CH}_2$). 3.85 – 3.93 (2H, para, $\text{ArOCH}_2\text{CH}_2$). 5.80 – 5.96 (m, 2H, *ArH*), 6.25 – 7.35 (m, 5H, *ArH*). A further two PS3CF additives were prepared by the same method – molecular weight analysis can be found in Table 1

Poly(isoprene) additives with 1CF group (PI1CF)

A typical PI1CF additive was prepared thus: Benzene (100 ml) and isoprene, (12.24 g, 0.18 mol) distilled from 0.1 ml *n*-BuLi immediately prior to use, were distilled under vacuum, into the reaction apparatus. For a target molecular weight of 3,000 g mol^{-1} , *s*-BuLi (2.91 ml of 1.4M solution, 4.08 mmol) was injected via a rubber septum. The solution was stirred at room temperature overnight, after which time the reaction was terminated by the injection of 1H,1H,2H,2H-perfluorodecyldimethyl chlorosilane (3.31 g, 6.12 mmol) and the reaction mixture was then left to stir overnight. The polymer was recovered by precipitation in excess methanol with a small amount of added antioxidant (BHT). The solvent was removed, the polymer redissolved in THF and reprecipitated into methanol, recovered and dried to constant mass in vacuo. Yield > 90%. M_n 4,900 g mol^{-1} , M_w 5,100 g mol^{-1} ; $^1\text{H NMR}$ (700MHz, CDCl_3 , δ , ppm): -0.04 – -0.07 (6H, $\text{Si}(\text{CH}_3)_2\text{CH}_2$), 0.70 (m, 3H, $\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 0.90 (m, 3H, $\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$). A further three PI1CF additives were prepared by the same method – molecular weight analysis can be found in Table 1.

Poly(isoprene) additives with 3CF groups (PI3CF)

A single PI3CF additive was prepared as described above for PS2CF with some modifications. Thus; hexane (50 ml) and isoprene (5.00 g, 0.07 mol), distilled from 0.1 ml *n*-BuLi immediately prior to use, were distilled, under vacuum, into the reaction apparatus. For a target molecular weight of 10,000 g mol^{-1} , *s*-BuLi (0.36 ml, 0.5 mmol) was injected via a rubber septum and the solution was stirred at room temperature for two days. In order to remove any possible unreacted monomer from the reaction mixture, the reaction solvent was distilled from the reaction vessel and replaced with fresh, dry hexane. This process was repeated two further times, before dissolving the living polymer in 25 ml of fresh hexane. A small sample of polymer solution (for molecular weight/NMR analysis) was removed and quenched with nitrogen sparged methanol. Meanwhile, a mixture of diphenylethylene (DPE) and tetramethylethylene diamine (TMEDA) (1.5 and 2 mol equivalents respectively with respect to BuLi) was prepared in a 50 ml flask fitted with a rubber septum. The contents of the flask were frozen with liquid nitrogen and the air evacuated. Upon warming to room temperature the vessel was raised to atmospheric pressure with dry nitrogen and *sec*-BuLi solution added dropwise to titrate out any remaining impurities. It was concluded that the mixture was free of impurities when a persistent reddish colour of diphenylhexyllithium was observed. The mixture of purified DPE/TMEDA was then injected to the living poly(isoprenyl)lithium and the mixture stirred at room temperature for 3 days, after which time the solution had developed an orange/red colour; a small sample was collected and quenched with nitrogen sparged methanol for analysis. To

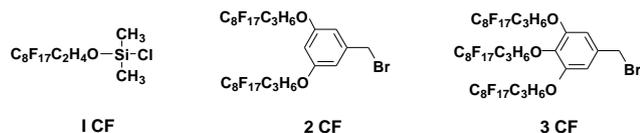


Figure 1. Chemical Structure of end capping agents

the DPE end capped living polymer was added THF (25 ml) by distillation using a CO₂/acetone bath. Meanwhile, in a separate 25 ml round bottom flask, 3,4,5-(tri-3-(perfluorooctyl)propyloxy)benzyl bromide (0.96g, 0.6 mmol, 1.2 equiv w.r.t lithium), purified as described previously, was dissolved in 10 ml dry THF. The THF solution of the end capping agent was then cooled in a CO₂/acetone bath and then added to the living DPE end capped poly(isoprene) solution at -78° Celsius. The orange colour of the living polymer slowly dissipated and after half an hour any remaining living chains were terminated with nitrogen sparged methanol. The polymer was recovered by precipitation in excess methanol containing a small amount of BHT. The solvent was removed, the polymer redissolved in THF and reprecipitated into methanol, recovered and dried to constant mass in vacuo. Yield > 90%. M_n 10,900 gmol⁻¹, M_w 11,200 gmol⁻¹; ¹H NMR (700MHz, CDCl₃, δ, ppm): 3.28 – 3.39 (2H, ArCH₂), 3.65 – 3.73 (m, 4H, meta, ArOCH₂CH₂), 3.87 – 3.95 (2H, para, ArOCH₂CH₂), 5.71 – 5.80 (m, 2H, ArH) (c), 4.92 – 5.27 (m, 1H, CH₂CH=C(CH₃)CH₂).

Results and Discussion

Synthesis of End Functionalised Polymer Additives.

We have previously described the synthesis of a limited number of similar polymer additives by atom transfer radical polymerisation⁴⁹ and ring opening polymerisation⁴⁷ in which the multifunctional end group was introduced through the use of a functionalised initiator. However, the sensitivity of living anionic polymerisation to functionality and impurities, limits the use of functionalised initiators and it was concluded that any methodology to synthesise end functionalised polymers of the type described herein, would be more productive if an end capping strategy was adopted. To this end, a series of end capping agents were used, with one, two or three C₈F₁₇ fluorocarbon (CF) groups (see figure 1). End capping agent 1CF (fig 1) is commercially available whereas 2CF and 3CF were synthesised according to previously reported procedures⁴⁹. Thus, a series of end functionalised polymers were prepared from both poly(styrene) (PS) and poly(isoprene) (PI). The synthesis of both PS and PI additives using 1CF end capping agent follows well known and previously described methods⁵². PS1CF and PI1CF functionalised additives were prepared with molecular weights from 6,000 – 40,000 gmol⁻¹ and molecular weights are reported in Table 1. In the case of PI1CF additives the constant error between target and actual molecular weight was subsequently found to be due to the use of a bottle of initiator which had been contaminated and therefore the concentration of active lithium was less than the 1.4M indicated. In general,

Table 1. Molecular weight and extent of successful end capping for a series of poly(styrene) (PS) and poly(isoprene) (PI) additives carry one (1CF), two (2CF) or three (3CF) C₈F₁₇ fluoroalkyl groups.

Additive	Target MW/gmol ⁻¹	M _n /gmol ⁻¹	M _w /gmol ⁻¹	% end capping*
PS1CF6K	5,000	5,700	6,000	87
PS1CF11K	10,000	11,500	11,800	74
PS1CF24K	20,000	23,600	24,300	87
PS1CF40K	50,000	39,300	40,600	96
PS2CF5K	5,000	4,900	5,100	79
PS2CF9K	10,000	9,000	9,400	63
PS2CF20K	20,000	19,500	20,100	62
PS2CF44K	50,000	43,700	44,800	60
PS3CF10K	10,000	10,100	10,400	78
PS3CF28K	20,000	27,600	28,100	43
PS3CF44K	50,000	43,500	44,400	76
PI1CF5K	3,000	5,900	6,400	80
PI1CF10K	6,000	10,500	10,500	83
PI1CF17K	10,000	17,100	17,700	82
PI1CF33K	20,000	33,300	33,400	67
PI3CF11K	10,000	10,900	11,200	50

* Extent of end capping calculated using ¹H NMR.

the endcapping reaction resulted in greater than 80% end functionalisation of chains and that the end capping reaction was not quantitative can almost certainly be attributed to the introduction of traces of impurities with the end capping agent.

The synthesis of additives, end functionalised with 2CF and 3CF end capping agents was a little more involved since the end capping of polymers produced by living anionic polymerisation with alkyl halides (and derivatives) is often complicated by unwanted side reactions such as lithium-halogen exchange reactions and Wurtz coupling⁵³. In the case of end capping polystyryllithium, the addition of a polar solvent such as THF to the reaction solvent and a reduced reaction temperature of -78° Celsius has been shown to have a positive impact on suppressing these side reactions and proved sufficient in this case^{54,55}. Using this approach, PS2CF and PS3CF additives were prepared with molecular weights in the range of 5,000 – 44,000 gmol⁻¹ (see table 1). Monomodal, narrow molecular weight distributions resulted (no chain coupling) and the extent of chain end functionalisation in some cases approached 80%. In other cases though, the extent of end capping was as low as 60-63% (PS2CF9K, PS2CF20K and PS2CF44K). These were some of the earliest end capping experiments attempted and despite our best efforts to purify the end capping agent, we suspect that impurities were probably introduced with the end capping agent, resulting in termination of a proportion of the living chain ends. The end capping agent cannot be distilled – it is a solid – so was purified by azeotropic drying with benzene. However, in order to transfer the ‘purified’ 2CF end capping agent into the reaction flask it was necessary to do so by injection, which involved introducing nitrogen gas into the flask. We suspect that this may be the primary source of the impurities. This methodology was altered for the synthesis of the PS3CF additives with the use of a modified reactor. In this case the 3CF end capping agent could be purified in the same way as the 2CF species but could be added directly to the main

reaction flask without the need to introduce nitrogen gas. As a result it can be seen that PS3CF10K and PS3CF44K were successfully end capped with improved extents of functionalisation of 78% and 76% respectively. However, to totally exclude all impurities from an end capping reaction of a polymer produced by living anionic polymerisation with such a large and complex end capping agent is extremely challenging! The relatively low extent of end capping for PS3CF28K was due to a miscalculation of the quantity of end capping agent necessary, with less than half the required amount added.

However, when the above described (successful) reaction conditions were applied to the end capping of living poly(isoprene) with the benzyl bromide derivative, 3CF, the resulting polymer showed a very low degree of end capping and a high degree of chain coupling. The propagating species at the chain end of polystyrene is a secondary (benzyl) carbanion whilst the propagating species of poly(isoprene), assuming high 1,4-microstructure, is a primary carbanion. Primary carbanions are more basic/nucleophilic than the styryl anion, and therefore more likely to undergo proton abstraction (leading to Wurtz coupling) during end capping reactions, despite the addition of THF and reduced temperatures. It was therefore necessary to reduce the basicity/nucleophilicity of the propagating chain end prior to the addition of the end capping agent. It has been shown that the most effective way of achieving this is to end cap the living polymer chain with diphenylethylene (DPE) prior to reaction with a benzyl halide⁵⁶. DPE will react with a living carbanionic chain end as a monomer but due to its steric bulk will not undergo homopolymerisation⁵⁷. The result is the introduction of a single DPE unit whilst retaining the living nature of the polymeric chain end. Addition of the 3CF end capping agent to the DPE end capped poly(isoprene) did not result in the undesirable side reactions and no chain coupling was observed. However, the extent of end capping was still modest (50%) in comparison to the analogous poly(styrene) additives. We suspect that this lower degree of end capping was due to a combination of impurities and possibly, premature termination of the reaction. When end capping poly(styrene), the orange colour of the living chain ends dissipated immediately, however the living DPE end group is less reactive and the reddish orange colour of the living DPE end capped poly(isoprene) dissipated much more slowly. It appeared as if the colour had disappeared after 30 minutes but it is possible that some living chains were terminated (prematurely) by the addition of methanol rather than by the desired end capping agent.

Analysis of Surface Properties

Analysis of surface properties was carried out on thin films of poly(styrene) and poly(isoprene) containing the described additives, to establish the relationship between the ability of the additives to modify the surface properties of the films and the molecular characteristics (molecular weight, number of CF groups and additive concentration) of the additives. Static contact angle measurements are a facile and convenient

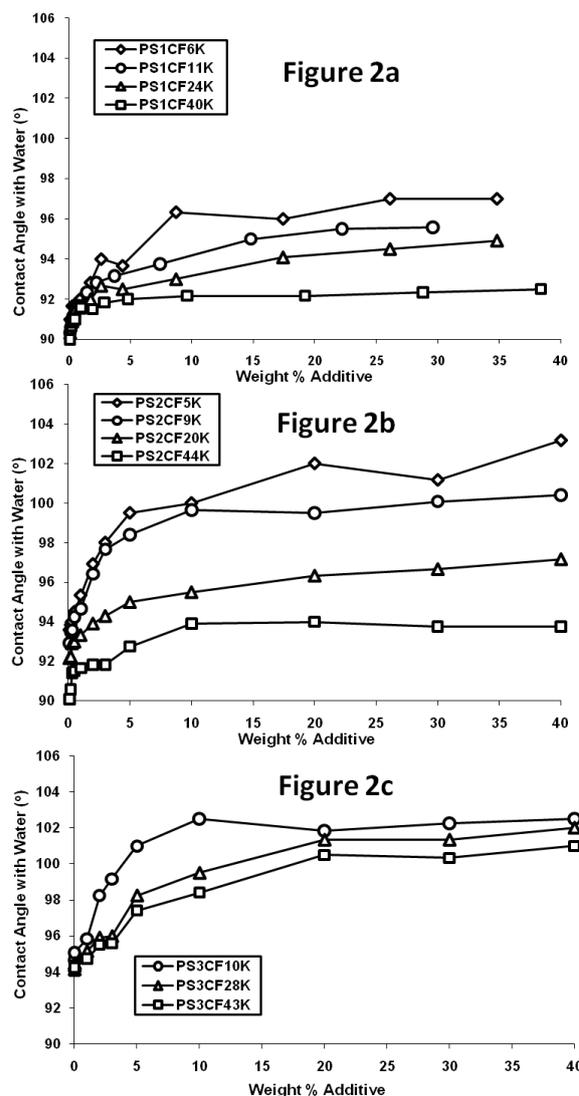


Figure 2. Effect of molecular weight and concentration of additive upon static contact angle with water on thin (unannealed) films of polystyrene containing PS1CF (Figure 2a), PS2CF (Figure 2b) and PS3CF (figure 2c) additives.

measure of the surface properties (hydrophobicity) of the films and contact angle analysis was carried out using water as the contact fluid. Measurements were initially carried out on 'as-spun' films and then repeated on films (of poly(styrene)) that had been annealed at 150° Celsius for a variety of times. Rutherford backscattering analysis was also carried out on examples of modified poly(isoprene) films to quantitatively analyse the effect of additive concentration and number of fluoroalkyl groups on the near surface elemental composition of the modified thin films.

Contact angle analysis – poly(styrene) additives

Contact angle measurements were carried out on thin films of 'bulk' polystyrene ($M_n = 90\,000\text{ g mol}^{-1}$, $M_w/M_n = 1.10$) containing various concentrations by weight of surface modifying additive. In each case the extent of end capping was considered when calculating the amount required to create a particular blend composition. It can be seen from the

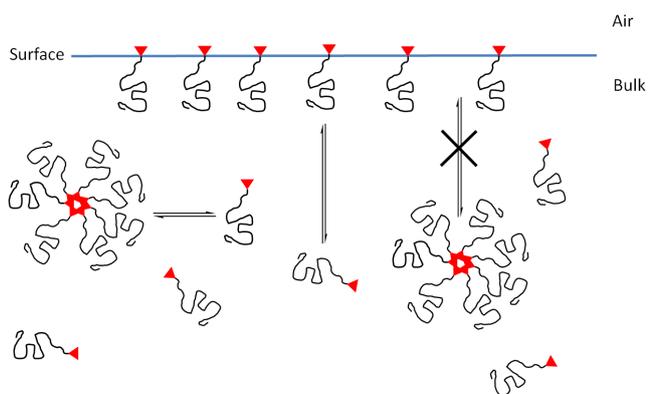


Figure 3. Schematic demonstrating proposed model of dynamic equilibria between free and aggregated additive chains in the bulk and between free additive chains in the bulk and at the surface

5 data in figure 2 that some very clear relationships emerge between both concentration of additive and the molecular parameters (molecular weight and number of CF groups) of the additive and surface properties. In all cases, increasing the concentration of additive leads to an initial sharp increase in contact angles at lower concentrations which is followed by a plateau in contact angle at higher concentrations of additive. That we observe significant changes to the surface properties compared to pure unmodified polystyrene on smooth spin cast films, implies strong surface segregation of the additives to the surface and that this segregation occurs during the spin coating process suggests high surface activity. The formation of a plateau or maximum contact angle might suggest that saturation of the surface with additive molecules has occurred, and the addition of further amounts of additive has little or no further impact upon the surface properties. However, the situation is somewhat more complex than that. That the fluorinated additives adsorb to the surface and generate an increase in contact angle is expected. The difference in surface energy between the two blend components allows the system to lower its overall free energy by having a surface enriched by the component with a lower surface energy – the fluorinated additive. As implied above, in reality, the distribution of a low surface energy component between bulk and surface, and therefore the surface composition, arises as a result of a series of interrelated phenomena and surface segregation of a low surface energy component can be hindered under specific conditions. For example, in a blend of block copolymer (with a low surface energy block) in a homopolymer matrix it has been demonstrated⁵⁸ that the block copolymer can behave in a manner similar to that of small molecule surfactants in solution, forming large aggregates which adsorb (diffuse) very slowly to the surface. We believe that there are also strong similarities in the behavior of the fluorinated additives reported here and surfactants in solution⁵⁹. Moreover, the formation of a plateau in contact angles at higher concentrations of fluorinated additive is likely to be due to the formation of aggregates of polymer additives in the bulk rather than saturation of additives at the surface. The fluorinated head groups are relatively

45 incompatible with the matrix poly(styrene) but at low concentrations the additives are molecularly dissolved – just as low concentrations of surfactants are in water. However, as the concentration of additives increases, there comes a point when the additives start to aggregate – just as surfactants form micelles! In the case of surfactants, the concentration at which this occurs is the critical micelle concentration (CMC); in the current work aggregation appears to occur above a critical aggregation concentration (CAC). In the case of surfactants, upon reaching CMC, the addition of further surfactant will serve only to increase the size and number of micelles and we suspect that above the CAC the addition of further additive merely results in an increase in the number/size of aggregates in the bulk phase. We have previously described similar behaviour⁵⁹ for an analogous polymer additive with a molecular weight of 10,000 g mol^{-1} carrying 2CF groups made from deuterated polystyrene (dPS2CF10K). Small-angle neutron scattering (SANS) data showed that this additive forms aggregates at higher concentrations when in a matrix of poly(styrene). At concentrations of up to 12 wt % of dPS2CF10K, good agreement existed between experimental scattering data and a random phase approximation (RPA) simulation for linear polymer chains – implying molecularly dispersed individual chains. However, at higher concentrations i.e. 15 and 20 wt %, large deviations were found between experimental data and a similar simulation for discrete chains. When a modified simulation was carried out, in which it was assumed that the polymer additives were present as aggregates resembling star polymers, an excellent fit between experimental data and simulation was observed. As a result, the fitted experimental data for 15 and 20 wt % dPS2CF10K in hPS suggested that aggregates existed with an average of 6 or 7 dPS2CF10K polymer chains per aggregate. This data supports the analogy that these fluorinated additives behave in a similar fashion to micelles in solution and it is certain that just as micelles are dynamic, there will be an equilibrium between free additive chains, molecularly dissolved in the bulk phase and aggregates (see figure 3). What is also certain is that the much larger aggregates will diffuse through the bulk at a much slower rate than the free chains and in effect only the free chains will be capable of surface segregation. There will also be an equilibrium between adsorbed chains at the surface and free chains in the bulk (in the presence of solvent or when above the glass transition temperature) and the distribution of additive chains between surface and bulk will be determined by both thermodynamic and kinetic factors, which in turn will be influenced by a number of parameters. The molecular weight of the additive will dictate the rate of diffusion through the bulk phase and the maximum packing density of additive chains at the surface. It is to be expected that low molecular weight additives will diffuse more quickly and pack more densely at the surface resulting in the higher contact angles observed for the lower molecular weight additives in figure 2. The number of CF groups will also play a huge role in this complex interplay of competing phenomena. Surface adsorption of the fluoroalkyl groups is thermodynamically favourable, leading to a reduction in the surface energy and

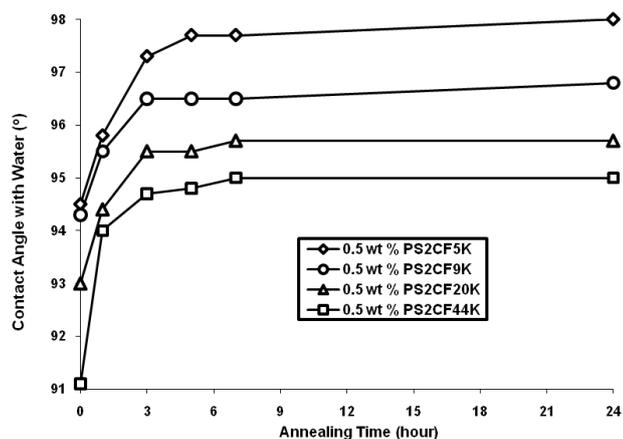


Figure 4. Effect of annealing time (150° C) on contact angle for PS2CF additives.

once an additive is adsorbed, desorption is inhibited by the thermodynamic sticking energy – the thermodynamic glue which keeps the additive at the surface⁵⁹. The sticking energy is related to the amount of reduction in surface energy which accompanies adsorption and therefore increasing the number of CF groups increases the sticking energy and further inhibits desorption. However, as the density of surface adsorbed chains increases we would expect an accompanying loss of conformational entropy and hence there is an entropic barrier to adsorption which competes with the sticking energy/reduction in surface energy. It is therefore expected that increasing the number of CF groups per additive chain, would result in a greater reduction in surface energy, driving the equilibrium distribution of chains in the system towards surface segregation and a concomitant increase in contact angles – as observed in figure 2. If we compare the observed contact angles for 3 additives of (nearly) identical molecular weight with 1, 2 and 3 CF groups, PS1CF11K, PS2CF9K and PS3CF10K and at a constant concentration of 10 wt% we can see that the contact angle increases from 94° (1CF) to 99.5° (2CF) to 102.5° (3CF).

Annealing of polystyrene thin films

It is highly unlikely that the distribution of additive chains in a thin film reaches equilibrium during the very short duration of the spin coating process. In order to establish the contact angle at equilibrium, films containing three concentrations of additive (from 0.5 – 5 wt %) were annealed at 150° Celsius (well above the glass transition temperature of poly(styrene) – 104° Celsius) for a variety of annealing times. At this temperature the polymer chains are mobile and the films are able to reorganise, allowing enhanced surface segregation driven by a reduction in surface energy. The data in figure 4 shows the impact of annealing on films containing 0.5 wt% of the PS2CF additives and this data is typical. It can be seen that for all four molecular weights, annealing for up to three hours results in a significant increase in contact angle. Extended annealing beyond three hours results in further modest increases in contact angle and beyond seven hours at 150° C there is little further change in surface properties –

Table 2. Maximum contact angles achieved for series of poly(styrene) films, unannealed (containing up to 40% additive) and annealed films containing varying concentrations of PS1CF, PS2CF and PS3CF additives.

Additive	Maximum Contact Angle Achieved			
	Unannealed Film ^a	Conc of Additive in Film		
		0.5%	2%	5%
PS1CF6K	97.0	94.5	95.7	96.3
PS1CF11K	95.5	94.0	94.5	95.7
PS1CF24K	95.0	93.7	94.2	94.7
PS1CF40K	92.5	93.5	94.0	94.3
PS2CF5K	103.2	98.0	100.3	101.5
PS2CF9K	100.4	96.8	100.0	101.3
PS2CF20K	97.2	95.7	96.3	98.7
PS2CF44K	94.0	95.0	95.8	96.8
PS3CF10K	102.5	98.7	105.5	107.2
PS3CF28K	102.0	97.7	101.3	105
PS3CF43K	101.0	96.0	99.3	101.0

^amaximum contact angle achieved for unannealed films containing up to 40% additive (see figure 2)

suggesting the system has reached equilibrium. What is remarkable is that annealing films containing very small quantities of additive (0.5%) can result in contact angles comparable to unannealed films containing substantially greater concentrations of additive. For example, annealing a film containing 0.5% PS2CF5K results in an equilibrium contact angle of approximately 98 degrees. To generate similar surface properties in an unannealed film requires approximately 6 times as much additive. Furthermore, in some cases annealing a film containing a relatively small quantity of additive can result in contact angles which exceed those achieved at all concentrations of additive in unannealed films. Thus comparing the data in figures 4 and 2b we can see that the maximum contact angle achieved in unannealed films containing up to 40 wt% of PS2CF44K is approximately 94 degrees whereas annealing a film containing as little as 0.5% of the same additive generates contact angles of almost 95 degrees and annealing a film containing 5% PS2CF44K results in a contact angle of nearly 97 degrees. The comparative differences in contact angle under discussion are modest and the errors associated with contact angle analysis should not be ignored. To minimise the error and maximise our confidence in these data, each contact angle data point is the average of at least three and in most cases six individual contact angle measurements. In our experience the error in measuring contact angles is rarely higher than +/- one degree and statistical analysis of the contact angle data indicated that the standard deviation for any given data point was, in the majority of cases, between 0.3 and 0.7. To display error bars on each data point would unnecessarily clutter the figures, however an error bar representing a typical standard deviation of 0.5 has been added to figure 4 for illustrative purposes. Although the error in any given data point is in some cases comparable to the difference between data sets, we are confident that the trends observed are genuine and reproducible and figure 4 clearly shows that annealing films containing small quantities of additive has a dramatically beneficial impact on surface properties. The advantage of

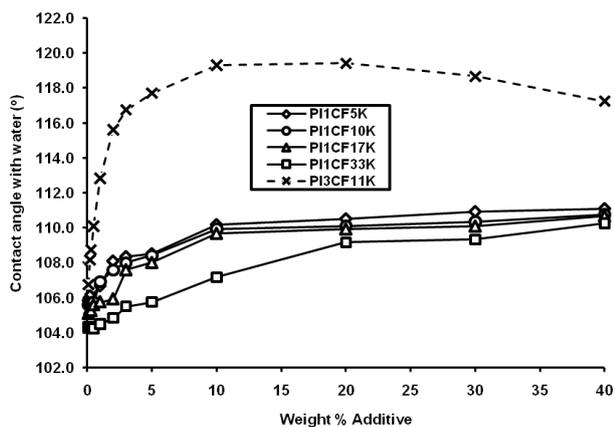


Figure 5. Effect of molecular weight and concentration of additive upon static contact angle with water on thin films of polyisoprene containing PI1CF and PI3CF additives

annealing films containing low concentrations of additive to allow them to reach equilibrium over simply adding greater quantities of additive is further demonstrated by the data in Table 2. In many cases, annealing films containing 5% (or less) results in contact angles in excess of those achieved by adding ever increasing amounts of additive into a film which is subsequently not annealed. Most dramatic are the results for PS3CF10K where annealing a film containing 5% of this additive results in a contact angle of 107 degrees – 5 degrees higher than that achieved in an unannealed film containing up to 40% additive, 17 degrees higher than unmodified poly(styrene) and approaching the surface properties of PTFE⁴⁹.

Contact angle analysis – poly(isoprene) additives

Contact angle measurements were also carried out on thin films of matrix poly(isoprene) ($M_n = 88,400 \text{ g mol}^{-1}$, $M_w/M_n = 1.02$) containing various concentrations by weight of PI surface modifying additives. In each case the extent of end capping was considered when calculating the amount required to create a particular blend composition. It can be seen from the data in figure 5 that similar relationships emerge between surface properties and the concentration, molecular weight and number of CF groups of the additive. In all cases increasing the concentration of additive leads to a concomitant increase in contact angles until a plateau in contact angles at higher concentrations of additive is observed. That we observe significant changes to the surface properties compared to unmodified poly(isoprene) implies strong surface segregation of the additives to the surface. The principal difference between the modified poly(styrene) and poly(isoprene) films is that poly(isoprene) is well above the glass transition temperature at room temperature and as such, in the case of poly(isoprene) the distribution of additive molecules between surface and bulk is able to reach equilibrium at room temperature. Thus the data in figure 5 was obtained from films which had been dried for 24 hours in vacuo at room temperature after spin coating. We are satisfied that that this data represents the equilibrium additive distribution since similar contact angle measurements taken over a 15 day

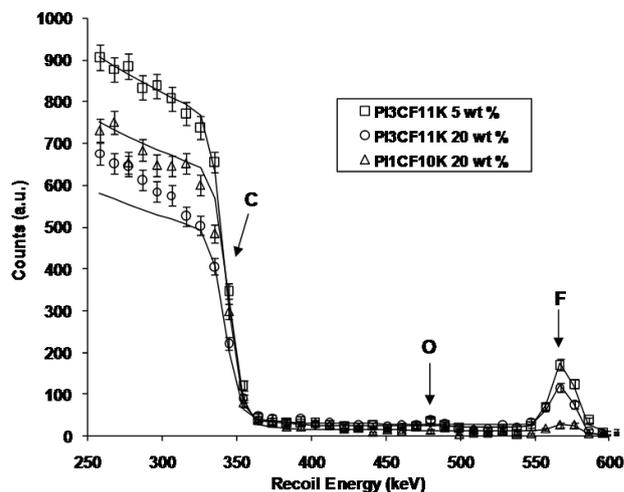


Figure 6. RBS data and simulations for poly(isoprene) films modified with 5 wt % PI3CF11K, 20 % PI3CF11K and 20 % PI1CF10K.

period revealed no change in surface properties. The data in figure 5 also shows a steady yet modest increase in contact angle with decreasing molecular weight of PI1CF additive but more dramatically shows the impact of the number of CF groups on surface properties. We can see that by comparing PI1CF10K and PI3CF11K, the additive with 3CF groups has a contact angle which is approximately 10 degrees higher than that of an additive of nearly identical molecular weight with only 1CF group – these differences reinforce the dramatic impact of the effect of the number of CF groups upon surface properties seen for PS additives in this work and previously⁴⁹. Moreover, it is noteworthy that when additive PI3CF11K is present at concentrations above 2%, the contact angle exceeds that of PTFE (approximately 110 degrees⁴⁹) by several degrees. One further important point to consider when measuring contact angles on films of poly(isoprene), is that since poly(isoprene) is above its glass transition temperature at room temperature, the film is able to reorganise in response to being in contact with water. Clearly the surface of both the unmodified and surface modified poly(isoprene) are highly hydrophobic and when placed in contact with water, the polymer chains in direct contact with the water droplet will attempt to minimise the interfacial tension and diffuse away from the surface. The concept of surface reorganisation in response to a new environment is well understood and has been previously described in the literature⁶⁰. The reorganisation would be expected to remove the CF groups from the interface and the contact angle decays over time. Indeed it is necessary to carry out the contact measurement immediately since the reorganisation of the films occurs in a matter of minutes and the contact angles decay steadily for a period of up to 45 minutes (the duration of the experiment). Whilst it might be argued that the decay in contact angle is due to evaporation of the solvent we don't believe this is the case even though the droplet of water was clearly evaporating. Evaporation of a droplet from a solid surface can result in a decay in contact angles, however it has been shown that when the liquid droplet is in contact with a non wetting surface such

as water on PTFE, evaporation results in a small (3-4 degrees) but rapid reduction in contact angle followed by a sustained period where evaporation occurs with a constant contact angle^{61,62}. In the present work the contact angle decayed at an almost constant rate over 45 minutes suggesting the reorganisation of the film surface. Intriguingly the rate of decay in contact angle also showed a strong dependence on the concentration of additive; this data will be the subject of a future publication.

Rutherford Back Scattering Analysis

Although contact angle analysis is a very useful method of analysing surface properties, it is only an indirect method of analysis of the surface chemistry. In order to obtain quantitative analysis of the near surface elemental composition of the modified films, Rutherford backscattering analysis (RBS) was carried out on examples of modified poly(isoprene) films. This analysis enables an examination of the effect of additive molecular weight and number of fluoroalkyl groups on the surface segregation and resulting surface composition of the modified thin films, confirming the relationship between these additive molecular parameters, surface adsorption and surface properties. The resulting data is therefore complementary to the contact angle data. RBS analysis was carried out on modified poly(isoprene) films containing 5 wt % PI3CF11K, 20 % PI3CF11K and 20 % PI1CF10K and the data shown in figure 6. The elemental markers in figure 6 indicate the maximum recoil energy of ⁴He⁺ ions from each element on the surface and since fluorine is the most massive element on the polymer surface, ⁴He⁺ recoils were detected at higher energy (570 keV) for fluorine, than recoils from other elements such as carbon and oxygen. The data in figure 6 for each film shows a step in the detected counts for carbon in each film and the height of the carbon step can be used to normalize the data since the amount of carbon in the polymer film is known. It is therefore the size of the fluorine peak relative to the carbon signal that allows us to determine the amount of fluorine at the surface. At first glance, it would appear that of the three peaks arising from the presence of fluorine (at approximately 570 keV), the film containing 5 wt % PI3CF11K has the highest concentration of fluorine. However, although the fluorine peak for the film containing 5% PI3CF11K appears to be larger than film containing 20% of the same additive it must be remembered that it is the size of this peak relative to the carbon signal at 350 keV that is important. RBS analysis can quantify fluorine adsorbed at the surface by providing a direct measurement in comparison to the bulk concentration. Simulations, in which the RBS spectrum of a thin layer of C₈F₁₇ on a thick film of poly(isoprene) were obtained, and are also shown in figure 6 (solid lines). Simulations were carried out using the SIMNRA program⁶³ and Rutherford scattering cross sections. The thickness of the appropriate C₈F₁₇ layer was allowed to vary to provide the best fit to the relevant experimental data, and the surface concentration of fluorocarbon from this layer was determined. When the appropriate amount of fluorine due to the bulk concentration of additive was included in the simulation, excellent agreement between simulation and data

Table 3. Calculated surface concentration of C₈F₁₇ groups in modified poly(isoprene) films containing 5 wt % PI3CF11K, 20 % PI3CF11K and 20 % PI1CF10K additive.

Sample	Surface concentration C ₈ F ₁₇ groups (mg/m ²)	Surface concentration C ₈ F ₁₇ groups (molecules/nm ²) ^a
20 wt % PI1CF10K	0.14	0.2
5 wt % PI3CF11K	0.86	1.24
20 wt % PI3CF11K	0.95	1.36

^aThese values are derived from the previous values of unit molecules/nm².

in the energy range 300-600 keV was observed. Moreover, we can convert the apparent thickness of C₈F₁₇ surface layer in the SIMNRA simulation to a surface concentration of adsorbed fluorocarbon groups per unit area. The surface concentration of C₈F₁₇ fluorocarbon groups obtained for each film are shown in table 3. It can be clearly seen from the data that the film containing 20 wt% PI3CF11K has the highest surface concentration of fluoroalkyl groups, which is followed closely by the film containing 5 wt% of the same additive. The film containing 20 wt% of an additive with nearly identical molecular weight but only 1 CF group (PI1CF10K) has a significantly lower surface concentration of fluoroalkyl groups and confirms the dramatic impact that varying the number of CF groups can have. This data is consistent with the contact angle data shown in figure 5 where it can be seen that there is a significant difference in contact angle between PI3CF and PI1CF additives of the same molecular weight and rather more modest differences between the contact angle between films containing 5 wt% and 20 wt% of PI3CF11K. Furthermore, if one assumes that the C₈F₁₇ fluorocarbon groups lie parallel to the film surface, then each has an effective surface area of 0.65 nm²⁴⁷. In this orientation, the surface concentrations of additive molecule in each film correspond to a surface coverage of C₈F₁₇ groups of 13 %, 81 % and 88 % for 20 wt% PI1CF10K, 5 wt% PI3CF11K and 20 wt% PI3CF11K respectively. At both concentrations of PI3CF we can see that the polymer film was covered with 80 – 90 % fluorocarbon. It is clear from the RBS analysis results that the derived surface concentrations are consistent with the contact angle analysis and confirm that the blend surfaces are highly fluorinated and either increasing the number of fluoroalkyl groups or increasing the concentration of additive results in a greater density of fluorine at the surface.

Conclusions

We describe here the development of synthetic methodologies to allow the synthesis, by living anionic polymerisation of a series of multi-end functionalised polymer additives, with 1, 2 and 3 fluoroalkyl groups, designed for the modification of polymer surfaces. Polymer additives were prepared from both poly(styrene) and poly(isoprene) with molecular weights in the range of 5,000 – 50,000 g mol⁻¹. We have reported that increasing the additive concentration and/or number of CF groups results in enhanced hydrophobicity whereas increasing the molecular weight of additive had the opposite effect. The distribution of a low surface energy additive between the bulk and the surface of a film, and therefore the surface

composition, arises as a result of a series of interrelated phenomena and we have argued that there are similarities in the behavior of the fluorinated additives studied in this work and surfactants in solution. Thus the formation of a plateau in contact angle (for unannealed films) at higher concentrations of fluorinated additive does not arise from saturation of the surface with additive but rather, is due to the formation of aggregates (analogous to micelles) of polymer additives in the bulk above a critical aggregation concentration. This argument is further supported by annealing studies, which in all cases result in an increase in surface segregation as evidenced by an increase in contact angle after annealing. Annealing allows the system to reach equilibrium and the distribution of additives at equilibrium will be dependent upon both an equilibrium between free additive chains in the bulk and aggregated chains in the bulk and a second equilibrium between free chains at the surface and free chains in the bulk

Poly(isoprene) has a glass transition temperature below room temperature and PI additives are able reach equilibrium without annealing at elevated temperatures. As a result of having a glass transition temperature below room temperature, PI films are able to reorganise in the presence of a droplet of water and contact angles were seen to decay steadily over time. In view of the fact that contact angle data cannot propose any quantitative information on surface elemental composition, we have also carried out Rutherford backscattering analysis to quantify the concentration of fluorine near the surface of the film with respect to blend compositions that containing 1CF and 3CF polyisoprene additives. It is clear that when only 1CF group is present, the concentration of fluorine at the surface is low. However, for an equivalent concentration (20 %) of additive and molecular weight of 3CF additive, the increase in functional groups results in approximately 90 % coverage of fluoroalkyl groups at the surface. Moreover, even a far lower concentration (5 wt%) of the same additive can result in greater 80% surface coverage. RBS provides quantitative data which is complimentary to the contact angle data in so much that it confirms that increasing the number of fluoroalkyl groups or increasing concentration results in an significant increase in the concentration of fluorine at the surface but that it is the number of fluoroalkyl groups that has the greatest impact on surface properties.

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Notes and references

- 1 L. J. Ward, J. P. S. Badyal, A. J. Goodwin and P. J. Merlin, *Polymer* 2005, **46**, 3986.
- 2 T. S. Cheng, H. T. Lin and M. J. Chuang, *Mat. Lett.* 2004, **58**, 650.
- 3 E. Selli, G. Mazzone, C. Oliva, F. Martini, C. Riccardi, R. Barni, B. Macandalli and M. R. Massafra, *J. Mater. Chem.* 2001, **11**, 1985.
- 4 S. Sigurdsson and Shishoo, *J. Appl. Polym. Sci.* 1997, **66**, 1591.
- 5 T. Kawase and H. Sawada, *J. Adhesion Sci. Tech.* 2002, **16**, 1121.

- 6 T. Kawase, M. Yamane, T. Fuji and M. Minigawa, *J. Adhesion Sci. Tech.* 1997, **11**, 1381.
- 7 S. Biltresse, D. Deschamps, T. Boxus and J. Marchand-Brynaert, *J. Polym. Sci., Pt A: Polym. Chem.* 2000, **38**, 3510.
- 8 D. L. Schmidt, C. E. Coburn, B. M. DeKoren, G. E. Potter, G. F. Meyers and D. A. Fischer, *Nature* 1994, **368**, 39.
- 9 S. Saïdi, F. Guittard, C. Guimon and S. G eribaldi, *Macromol. Chem. Phys.* 2005, **206**, 1098.
- 10 A. Mueller, T. Kowalewski and K. L. Wooley, *Macromolecules* 1998, **31**, 776.
- 11 D. J. Gan, A. Mueller and K. L. Wooley, *J. Polym. Sci., Pt A: Polym. Chem.* 2003, **41**, 3531.
- 12 C. S. Gudipati, C. M. Greenleaf, J. A. Johnson, P. Prayongpan and K. L. Wooley, *J. Polym. Sci., Pt A: Polym. Chem.* 2004, **42**, 6193.
- 13 C. S. Gudipati, J. A. Finlay, J. A. Callow, M. E. Callow and K. L. Wooley, *K. L. Langmuir* 2005, **21**, 3044.
- 14 C. Cheng, K. L. Wooley, and E. Khoshdel, *J. Polym. Sci., Pt A: Polym. Chem.* 2005, **43**, 4754.
- 15 K. T. Powell, C. Cheng, K. L. Wooley, A. Singh and M. W. Urban, *J. Polym. Sci., Pt A: Polym. Chem.* 2006, **44**, 4782.
- 16 D. R. Iyengar, S. M. Perutz, C. A. Dai, C. K. Ober and E. J. Kramer, *Macromolecules* 1996, **29**, 1229.
- 17 A. Boker, K. Reihls, J. G. Wang, R. Stadler and C. K. Ober, *Macromolecules* 2000, **33**, 1310.
- 18 M. L. Xiang, X. F. Li, C. K. Ober, K. Char, J. Genzer, E. Siviniah, E. J. Kramer and D. A. Fisher, *Macromolecules* 2000, **33**, 6106.
- 19 J. Genzer, E. Siviniah, E. J. Kramer, J. G. Wang, M. L. Xiang, K. Char, C. K. Ober, R. A. Bubeck, D. A. Fischer, M. Graupe, R. Colorado, O. E. Shmakova and T. R. Lee, *Macromolecules* 2000, **33**, 6068.
- 20 T. Hayakawa, J. G. Wang, M. L. Xiang, X. F. Li, M. Ueda, C. K. Ober, J. Genzer, E. Siviniah, E. J. Kramer and D. A. Fischer, *Macromolecules* 2000, **33**, 8012.
- 21 L. Andruzzi, E. Chiellini, G. Galli, X. F. Li, S. H. Kang and C. K. Ober, *J. Mater. Chem.* 2002, **12**, 1684.
- 22 X. F. Li, L. Andruzzi, E. Chiellini, G. Galli, C. K. Ober, A. Hexemer, E. J. Kramer and D. A. Fisher, *Macromolecules* 2002, **35**, 8078.
- 23 J. P. Youngblood, L. Andruzzi, C. K. Ober, A. Hexemer, E. J. Kramer, J. A. Callow, J. A. Finlay and M. E. Callow, *Biofouling* 2003, **19**, 91.
- 24 A. Hexemer, E. Siviniah, E. J. Kramer, M. Xiang, X. Li, A. Fischer and C. K. Ober, *J. Polym. Sci., Pt B: Polym. Phys.* 2004, **42**, 411.
- 25 E. Martinelli, S. Menghetti, G. Galli, A. Glisenti, S. Krishnan, M. Y. Paik, C. K. Ober, D. M. Smilgies and D. A. Fischer, *J. Polym. Sci. Pol. Chem.* 2009, **47**, 267.
- 26 G. Galli, A. Ragnoli, M. Bertolucci, C. K. Ober, E. J. Kramer and E. Chiellini, *Macromol. Symp.* 2004, **218**, 303.
- 27 G. Galli, E. Martinelli, E. Chiellini, C. K. Ober and A. Glisenti, *Mol. Crystals and Liquid Crystals* 2005, **441**, 211.
- 28 S. Krishnan, N. Wang, C. K. Ober, J. A. Finlay, M. E. Callow, J. A. Callow, A. Hexemer, K. E. Sohn, E. J. Kramer and D. A. Fischer, *Biomacromolecules* 2006, **7**, 1449.
- 29 S. Krishnan, R. Ayothi, A. Hexemer, J. A. Finlay, K. E. Sohn, R. Perry, C. K. Ober, E. J. Kramer, M. E. Callow, J. A. Callow and D. A. Fischer, *Langmuir*, 2006, **22**, 5075.
- 30 S. Krishnan, M. Y. Paik, C. K. Ober, E. Martinelli, G. Galli, K. E. Sohn, E. J. Kramer and D. A. Fischer, *Macromolecules* 2010, **43**, 4733.
- 31 T. F. Schaub, G. J. Kellogg, A. M. Mayes, R. Kulasekere, J. F. Ankner and H. Kaiser, *Macromolecules* 1996, **29**, 3982.
- 32 S. J. McLain, B. B. Sauer and L. E. Firment, *Macromolecules* 1996, **29**, 8211.
- 33 W-K. Lee, I. Losito, J. A. Gardella, Jr. and W. L. Hicks, Jr. *Macromolecules* 2001, **34**, 3000.
- 34 Z. Su, D. Wu, S. L. Hsu and T. J. McCarthy, *Macromolecules* 1997, **30**, 840.
- 35 M. O. Hunt, A. M. Belu, R. W. Linton and J. M. DeSimone, *Macromolecules* 1993, **26**, 4854.
- 36 S. Affrossman, M. Hartshorne, T. Kiff, R. A. Pethrick, and R. W. Richards, *Macromolecules* 1994, **27**, 1588.

- 37 C. Yuan, M. Ouyang and J. T. Koberstein, *Macromolecules* 1999, **32**, 2329.
- 38 K. Tanaka, D. Kawaguchi, Y. Yokoe, T. Kajiyama, A. Takahara and S. Tasaki, *Polymer* 2003, **44**, 4171.
- 39 P. A. O'Rourke Muisener, S. K. Kumar and J. T. Koberstein, *Macromolecules* 2003, **36**, 771.
- 40 P. A. V. O'Rourke Muisener, C. A. Jalbert, C. Yuan, J. Baetzold, R. Mason, D. Wong, Y. J. Kim and J. T. Koberstein, *Macromolecules* 2003, **36**, 2956.
- 41 K. Sugiyama, A. Hirao and S. Nakahama, *Macromol. Chem. Phys.* 1996, **197**, 3149.
- 42 A. Hirao, G. Koide and K. Sugiyama, *Macromolecules* 2002, **35**, 7642.
- 43 A. Hirao, K. Sugiyama and H. Yokoyama, *Prog. Polym. Sci.* 2007, **32**, 1393.
- 44 A. A. El-Shehawey, H. Yokoyama, K. Sugiyama and A. Hirao, *Macromolecules* 2005, **38**, 8285.
- 45 H. Li, Y. M. Zhang, H. Zhang, M. Z. Xue and Y. G. Liu, *J. Polym. Sci., Pt A: Polym. Chem.* 2006, **44**, 3853.
- 46 L. R. Hutchings, A. P. Narriainen, R. L. Thompson, N. Clarke and L. Ansari, *Polymer International* 2008, **57**, 163.
- 47 L. R. Hutchings, A. P. Narriainen, S. M. Eggleston, N. Clarke and R. L. Thompson, *Polymer* 2006, **47**, 8116.
- 48 A. L. Narriainen, L. R. Hutchings, I. A. Ansari, N. Clarke and R. L. Thompson, *Soft Matter* 2006, **2**, 126.
- 49 A. P. Narriainen, L. R. Hutchings, I. Ansari, R. L. Thompson and N. Clarke, *Macromolecules* 2007, **40**, 1969.
- 50 R. L. Thompson, A. P. Narriainen, S. M. Eggleston, I. A. Ansari, L. R. Hutchings and N. Clarke, *Journal of Applied Polymer Science* 2007, **105**, 623.
- 51 F. T. Kiff, R. W. Richards and R. L. Thompson, *Langmuir*, 2004, **20**, 4465.
- 52 L. R. Hutchings, R. W. Richards, R. L. Thompson, D. G. Bucknall and A. S. Clough, *European Physical Journal E*, 2001, **5**, 451.
- 53 H. L. Hsieh and R. P. Quirk, *Anionic Polymerization, Principles and Practical Applications*; Marcel Dekker, Inc: New York, 1996.
- 54 M. Gauthier and M. Moller, *Macromolecules*, 1991, **24**, 4548.
- 55 R. A. Kee and M. Gauthier, *Macromolecules*, 1999, **32**, 6478.
- 56 C. M. Fernyhough, R. N. Young, A. J. Ryan and L. R. Hutchings, *Polymer*, 2006, **47**, 3455.
- 57 L. R. Hutchings, J. M. Dodds and S. J. Roberts-Bleming, *Macromolecules*, 2005, **38**, 5970.
- 58 Y. Lyatskaya, D. Gersappe, N. A. Gross and A. C. Balazs, *J. Phys. Chem.*, 1996, **100**, 1449.
- 59 I. A. Ansari, N. Clarke, L. R. Hutchings, A. Pillay-Narriainen, A. E. Terry, R. L. Thompson and J. R. P. Webster, *Langmuir*, 2007, **23**, 4405.
- 60 J. T. Koberstein, *J. Polym. Sci. Pt. B-Polym. Phys.*, 2004, **42**, 2942.
- 61 T. Furuta, A. Nakajima, M. Sakai, T. Isobe, Y. Kameshima and K. Okada, *Langmuir*, 2009, **25**, 5417.
- 62 G. McHale, S. M. Rowan, M. I. Newton and M. K. Banerjee, *J. Phys. Chem. B*, 1998, **102**, 1964.
- 63 M. Mayer, SIMNRA User's Guide, 9/113, Max-Planck-Institut für Plasmaphysik: Garching, 1997.

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