Systematic Comparison of Single-Walled Carbon Nanotube/ Polyvinyl Acetate *Graft-to* Reactions

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The covalent grafting of polymers to single-walled carbon nanotubes (SWCNTs) is widely used to improve solvent compatibility, as well as composite and functional performance. Here, three different *graft-to* strategies are directly compared, using azide, diazonium, and bromine terminated polymers, over four different molecular weights (oligomeric to 10 kDa) using specifically synthesized low polydispersity, end-group controlled polyvinyl acetate (PVAc) prepared by polymerisation using a bespoke protected-amine RAFT agent. Coupling of the bromo-polymer to reduced SWCNTs led to higher degrees of functionalisation (grafting ratios up to 68.9 %) than the azide and diazonium grafting reactions, attributed to better initial dispersion of the pre-grafted SWCNTs. The use of higher molecular weight polymers led to a decrease in the total weight of polymer grafted, as the increase in per-polymer weight is more than offset by steric occlusion on the SWCNT surface. For these *graft-to* reactions, the dispersibility of grafted SWCNTs was found to depend most strongly on the polymer molecular weight, not total weight of grafted polymer or grafting chemistry, with an intermediate M_n~5757 PVAc giving the best dispersibilities, at up to 118 mg L^{-1}.

1. Introduction

Single walled carbon nanotubes (SWCNTs) are attractive in many diverse areas of materials science, due to their exceptional mechanical,[1] thermal[2] and (opto)electronic[3] properties. However, in many cases, inherent processing challenges have hindered their large-scale use. Covalent functionalization of SWCNTs (f-SWCNTs) is a well-established route to increasing solubility/dispersibility, improving compatibility with other materials, and introducing new functionalities. Polymers are often grafted to SWCNTs to aid matrix dispersion and enhance stress transfer, but are also relevant to applications as diverse as imaging agents increasing *in vivo* imaging agents,[4] chemical sensors,[5] and crystallization nucleation agents.[6] Grafted polymers offer significant steric bulk and can significantly alter surface characteristics through only a low concentration of attachment points.

There are many strategies for the chemical modification of SWCNTs, including oxidative acid treatments, non-covalent physisorption of polymers and small molecules, and the covalent attachment of molecules using a range of common chemical reactions.[7] Whilst acid oxidation is popular and introduces carboxylic acids suitable for further reaction (often via ester/amidification), it causes significant damage to the SWCNT framework, forms vacancy defects which cannot be healed via annealing,[8] and introduces contaminating debris.[9] The severely diminished electronic[3] and mechanical[10] properties render this approach less suitable for the majority of, though not all, applications. Non-covalent physisorption (often with polyaromatics) causes no inherent damage to the SWCNT framework and can alter surface chemistry of the nanomaterial, however, the weak interactions are less attractive in many cases, especially for mechanical reinforcement in composites.

Direct covalent functionalisation of the SWCNT sidewall (without relying on initial defect formation) is, therefore, often preferred. Highly reactive species including carboradicals,[11]

nitrenes,[12] and azomethine ylides[7] are capable of functionalising the pristine, delocalized sp^2 framework of the nanotubes and are often synthesized *in situ* given their high reactivity and short lifetimes. Usually, SWNT bundles are ultrasonicated to increase the degree of dispersion and hence improve reagent access to the surface,[13] however, the SWCNTs are rarely fully individualized, and may be cut or damaged by the sonication.[14, 15]

While nitrenes are predominantly formed by degradation of azides, there are several routes used to form carboradicals, such as photolysis of iodides and *in situ* radical polymerization (using SWCNT functionalisation as a termination mechanism); however, the most common route relies on the degradation of diazonium salts.[16] An interesting alternative carboradical route uses of 'nanotubide': negatively charged SWCNT anions.[17] Although several mechanisms can be proposed for nanotubide functionalisation, single electron transfer, is the most commonly accepted.[18] In this mechanism, the charge on nanotubide is transferred to one of a large family of functionalities, most commonly organohalides; the resulting radical anion subsequently degrades to form a carboradical which reacts with the SWCNT. This route offers the important benefit that the SWCNTs can be spontaneously dissolved as individualized nanotubides in certain solvents[17,19] such as N,N-dimethylacetamide (DMAc), exposing the entire surface for the subsequent grafting reactions.

There are two overarching approaches to functionalizing SWCNTs with polymers; *graft-from* involves in situ polymerization from a specific initiating site bound to the SWCNT sidewall, while *graft-to* strategies couple pre-synthesised polymers to the SWCNT surface. The *graft-from* approach limits the ability to determine molecular weight and polydispersity index (PDI) after synthesis, making it challenging to analyze the underlying factors controlling the reaction. On the other hand, the grafting of bulky polymer molecules is usually sterically constrained, limiting the grafting stoichiometry (C/R, number of SWCNT framework carbons

per polymer chain) and thus grafting ratio (weight polymer as percentage relative to the SWCNT framework) for *graft-from* reactions.

The theory governing the grafting of polymers to flat (non-curved, infinite) surfaces is well established by the comprehensive works of de Gennes, detailing the relationship of polymer conformation, grafting density, and molecular weight.[20] While there are obvious overlaps, the curved and bundled nature of SWCNTs suggest distinct differences; to date, few studies have systematically considered the physical aspects of polymer grafting on SWCNTs. The most comprehensive study, by Chadwick *et al.* studied the *graft-to* reaction of azide-terminated polystyrene reacted with SWCNTs pre-functionalised with alkyne containing moieties.[21] The grafting ratio displayed a maximum at intermediate molecular weight, presumably due to the balance between the increasing weight of each polymer chain and steric occlusion of polymers already present at the surface, similar to de Gennes theory (though at lower absolute nominal coverage).; the dispersibility of grafted nanotubes was greatest for shorter polymer molecular weights. However, the use of the alkyne anchors intrinsically limits the number and location of the grafting sites and complicates a direct comparison to de Gennes theory. Further studies of *graft-to* reactions on SWCNTs are therefore of interest. In addition, the extent of grafting and the resulting dispersability may depend on the specific grafting chemistry, either due to intrinsic character of the bond formed or the reaction conditions required.

This study explores a series of reactions directly grafting monofunctional polymers to SWCNTs, using three alternative strategies for direct SWCNT modification, across a systematic series of molecular weights. Diazonium and azide terminated polymers represent macromolecular embodiments of two of the most common SWCNT sidewall chemistries; the third approach exploits the reaction of individual nanotubide ions with bromo-terminated polymers. A well-defined, low polydispersity, model polymer (polyvinyl acetate) with a single,

terminal, easy to manipulate end group allowed a consistent set of molecular weights to be studied in all three approaches.

2. Experimental

2.1 Materials

Single-walled carbon nanotubes (Elicarb PR929, batch 108511/g) were supplied by Thomas Swan Ltd (U.K.). 4-aminobenzylalcohol (98 %) was purchased from Fluorochem Ltd. (UK). Phosphorous pentoxide (>98%), di-*t*-butyl dicarbonate (>99%), pyridine (anhydrous, 99.8%), thionyl chloride (>99%), anhydrous ethanol (200 proof >99.5%), vinyl acetate (>99% with 3-20 ppm hydroquinone stabiliser), acetic acid (>99.8%), trifluoroacetic acid (TFA, 99%), 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%), lauroyl peroxide (Luperox® LP, 97%), sodium nitrite (99.999%), sodium azide (>99.5%), sodium (ingot, 99.99%), naphthalene (99%), bromoacetyl bromide (>98%), anhydrous N,N-dimethylacetamide (99.9%), triethylamide (TEA, >99%) and isoamyl nitrite (96%) were purchased from Sigma Aldrich Ltd. (U.K.). Potassium *O*-ethyl xanthate (98%) was purchased from Alfa Aesar (UK). Dichloromethane (DCM, 99.9%), n-hexane (99.9%), ethanol (96%), tetrahydrofuran (THF, 99.9%), petroleum benzene (petrol, 40-60 °C fraction), N,N-dimethylacetamide (99%), N,N-dimethylformamide (DMF, 99.7%, HPLC grade), sodium sulphate (>99%), sodium hydrogen carbonate (>98%), sodium hydroxide (99.9%), and calcium chloride (99%) were purchased from VWR UK Ltd. (U.K.). Argon (pureshield 99.9999%), piped nitrogen, and dry oxygen (custom 20/80 v/v oxygen nitrogen mix) were purchased from BOC gases (DE).

Vinyl acetate was distilled under reduced pressure to remove inhibitor and oligomers immediately before use. AIBN was recrystallized from methanol (1.5 g in 5 mL MeOH at 60 °C, cooling to RT over *ca.* 30 min) and collected via vacuum filtration as needle-like crystals before drying under vacuum for 1 h. The purified crystals were stored under argon at 0 °C in the absence of light, and used within a week of purification.. Anhydrous DMAc was dried

further with activated 4 Å molecular sieves (Sigma Aldrich) in a glovebox for 2 days prior to use. Naphthalene was dried under vacuum in the presence of P_2O_5 overnight before use. SWCNTs were also purified before use (*vide infra)*, and all other reagents were used as received and without additional purification. All work involving sodium, sodium naphthalide, and nanotubide was performed in a N_2 glovebox (mBraun, <0.1 pm O_2, <0.1 ppm H_2O) using oven dried glassware. All reactions were carried out under nitrogen unless otherwise stated with inert gases passed through a silica, calcium chloride and sodium hydroxide drying column before use. Purification over silica refers to flash column chromatography using Silica Gel 60 (VWR). Unless specified otherwise, filtration refers to the use of a Buchner funnel fitted to a water aspirator and using Whatman brand filter paper (VWR). 200 nm PTFE syringe filters and filter membranes were purchased from Whatman. PTFE membranes (100 nm pore size, hydrophilic) were purchased from Millipore (UK).

2.2 Characterisation

^{1}H NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometers as homogenous solutions and processed using Topspin software (Ver 1.3, by Bruker BioSpin). Deuterated solvents were purchased from VWR and used as received. d_H values are quoted to the nearest 0.01 ppm and coupling constants to the nearest 0.5 Hz. Spectra were calibrated to the non-deuterated solvent peak with peaks numbered according to Cahn-Ingold-Prelog rules.. NMR backbone analysis of polymer molecular weight was calculated from the relative integrals of the integrals of the polymer backbone peaks (δ = 1.55-2.10 ppm (5nH/monomer) and 4.66-5.10 ppm (nH/monomer)) and the less downshifted aromatic protons of the carbon β to the nitrogen (δ = 6.4 to 7.0 ppm, 2H), with the exception of acylbrominated **8** where the γ carbon's protons are used (δ = 7.5 ppm, 2H) to avoid the $CHCl_3$ signal.

UV-Vis spectra were recorded on a Perkin-Elmer Lambda 950 between 300–1200 nm using an optical glass 4 mm pathlength cuvette. Infra-red spectra were recorded on a Perkin-Elmer Spectrum 100 with a Universal ATR sampling accessory. Gel permeation chromatography was carried out using a Polymer Labs GPC 50 system with two PL-gel 5µ columns. Samples were eluted with DMF with 1% TEA and 1% acetic acid. The instrument was calibrated to PMMA standards. Data were processed using Polymer Labs Cirrus software. Centrifugation was carried out using a Sigma 2-16K centrifuge using fluorinated ethylene propylene centrifuge tubes (Thermo Fischer Scientific), with the neck sealed with PTFE tape in the thread when centrifuging nanotubide to avoid air ingress.

Thermogravimetric analysis was carried out using a Pyris 1 TGA, using 1–2 mg of sample, under nitrogen (60 sccm), heating at 100 °C for 60 min followed by a heating ramp to 700 °C at 10 °C min^{-1}. Weight of polymer in the sample were measured as the weight loss at 550 °C (above the degradation temperature of PVAc, ESI Fig. S1) minus the weight loss at 550 °C for the purified SWCNTs. Grafting ratios are presented as weight polymer as a percentage of SWCNT framework weight, calculated from the weight loss. Grafting stoichiometries (C/R, number of SWCNT framework carbons per polymer chain) were calculated using a SWCNT M_w of 12 Da and polymer M_n of the parent, amine/hydrogen-terminated polymer (**6**) minus 2 Da for azide grafting, minus 16 Da for diazonium grafting and plus 41 for bromide grafting (ESI, Table S3) to account for the different expected grafting mechanisms (Fig. 2). Instrumental errors are provided, calculated using the lower weight threshold (1 mg).

2.3 *Synthesis*

Preparation of t-butyl 4-(hydroxymethyl)phenyl carbamate (1).

4-aminobenzylalcohol (8.26 g, 67.2 mmol, 1.0 eq) was dissolved in in dry dichloromethane (500 mL) before di-*t*-butyl dicarbonate (17.0 g, 73.8 mmol, 1.1 eq) was added. The resulting solution was stirred for 18 h under nitrogen at room temperature, before removing the solvent under reduced pressure to leave a brown residue. This crude product was purified over silica (EtOAc/Hexane 1:1 (v/v), R_f 0.49) to give a white solid (10.7 g, 71.6%). ^{1}H NMR (CDCl$_3$), (400 MHz): δ_H = 1.53 (s, 9H, CH_3), 2.25 (br s, 1H, OH), 4.60 (s, 2H, PhCH_2), 6.72 (br s, 1H, NH), 7.27 (d, $^3J_{HH}$ 8.5 Hz, 2H, ArH^2), 7.34 (d, $^3J_{HH}$ 8.5 Hz, 2H, ArH^3).

Preparation of t-butyl 4-(chloromethyl)phenyl carbamate (2)

Pyridine (0.45 mL, 3.63 mmol, 0.09 eq) was added to a solution of alcohol **1** (9.00 g, 40.3 mmol, 1.0 eq) in DCM (300 mL), followed by thionyl chloride (6.44 g, 88.7 mmol, 2.2 eq). The resulting solution was stirred for 30 min followed by the addition of water (50 mL). The two phases were separated and the aqueous layer extracted with DCM (2 x 50 mL). The combined organics were dried over sodium sulphate, filtered and reduced to dryness to give an off-white solid (6.56 g, 68%). ^{1}H NMR (CDCl$_3$), (400 MHz): δ_H = 1.51 (s, 9H, CH_3), 4.54 (s, 2H, PhCH_2), 6.63 (br s, 0.91H, NH), 7.29 (d, $^3J_{HH}$ 8.0 Hz, 2H, ArH^2), 7.35 (d, $^3J_{HH}$ 8.0iiii Hz, 2H, ArH^3).

Preparation of S-(4-((t-butoxycarbonyl)amino)benzyl)-O-ethyl xanthate (3)

Chloride **2** (6.00 g, 24.8 mmol, 1.0 eq) was dissolved in dry ethanol (100 mL) under nitrogen with stirring. In one portion, potassium *O*-ethyl xanthate (4.39 g, 27.4 mmol, 1.1 eq) was added and the resulting suspension left to stir at room temperature for 18 h. After this time, the solvent was removed under vacuum to leave a pale yellow solid. Acetone (100 mL) was added and the suspension filtered through a sintered glass funnel. The filtrate was evaporated to dryness and the resulting solid recrystallized from ethanol to give pale yellow crystals (6.15 g, 76%). [1]H

NMR (CD$_3$)$_2$ CO), (400 MHz): δ_H = 1.42 (t, $^3J_{HH}$ 7.2 Hz, 3H, CH$_2$CH_3), 1.51 (s, 9H, CH_3C), 4.31 (s, 2H, PhCH_2), 4.65 (q, $^3J_{HH}$ 7.2 Hz, 2H, CH_2CH$_3$), 6.46 (br s, 0.91H, NH), 7.26 (d, $^3J_{HH}$ 8.0 Hz, 2H (overlaps CHCl$_3$), ArH^2), 7.30 (d, $^3J_{HH}$ 8.0 Hz, 2H, ArH^3).

RAFT polymerisation of vinyl acetate to yield "Xan-PVAc-NHBoc" (4)

In a typical procedure, a 100 mL polymerisation tube was sealed with a septum was which was then evacuated and refilled with nitrogen three times. Vinyl acetate (5.1 mL, 55.3 mmol, 60 eq.) was then added. After degassing three times with the freeze-pump-thaw method, the tube was refilled with argon and the septum exchanged for a PTFE screw top. The sealed tube was then heated to 80 °C before adding RAFT agent **3** (300 mg, 0.92 mmol, 1.0 eq) and AIBN (30 mg, 0.18 mmol, 0.2 eq.) to the mixture, and heating for the specified time. Solvent was removed under vacuum to afford crude polymer **4** (*ca.* 95%). ^{1}H NMR (CDCl$_3$), (400 MHz): δ_H = 1.44 (t, 3H, CH$_2$CH_3), 1.53 (s, 9H, (CH_3)$_3$C), 1.63-2.15 i(m, 5nH, CH_2CHOCOCH_3 (backbone)), 2.23 (br, 2H, CH_2CHOCOCH$_3$ (endgroup)), 4.65 (dd, 2H, CH_2CH$_3$), 4.77-5.30 (br m, nH, CH$_2$CHOCOCH$_3$ (backbone)), 6.49 (br s, 1H, NH), 6.61 (br m, 1H, CH$_2$CHOCOCH$_3$ (endgroup)), 7.06 (m, 2H, ArH^2), 7.25 (m, 2H, ArH^3). IR: v = 2976.7 (w), 2931.4 (w), 1730.6 (s; acetate C=O), 1530.0 (w; Boc C=O), 1433.1 (w), 1369.3 (m), 1227.0 (s; acetate C-O), 1115.3 (w), 1019.6 (s, acetate C-O), 943.79 (w), 769.6 (w), 604.03 (w).

Removal of xanthate groups to yield "H-PVAc-NHBoc" (5)

In a typical procedure, lauroyl peroxide (2.1 eq), xanthate-terminated polymer **4** (1.0 eq. of xanthate), THF (3 mL) and IPA (6 mL) were added to a polymerisation tube with a stirrer bar. After degassing three times with the freeze-pump-thaw method, the tube was refilled with argon and the septum exchanged for a PTFE screw top. The sealed tube was then heated at 80 °C for 18 h. After this time, the solution was evaporated to dryness and the residue dissolved

in the minimum amount of THF, then precipitated into petrol and left to settle overnight. The supernatant was decanted and the remaining solid dissolved in THF, transferred to a round-bottom flask and reduced to dryness under vacuum to give polymer **5** which was purified using precipitation from THF into petrol (40-60 °C fraction, >99%). ^{1}H NMR (CDCl$_3$), (400 MHz): δ_H = 1.44 (t, 3H, CH$_2$C*H$_3$*), 1.53 (s, 9H, (C*H$_3$)$_3$*C), 1.63-2.15 (m, 5nH, C*H$_2$*CHOCOC*H$_3$* (backbone)), 2.23 (br, 2H, C*H$_2$*CHOCOCH$_3$ (endgroup)), 4.09 (m, 2H, C*H$_2$*OCOCH$_3$), 4.77-5.30 (br m, nH, C*H$_2$*CHOCOCH$_3$ (backbone)), 6.53 (br s, 1H, N*H*), 7.09 (m, 2H, Ar*H^2*), 7.28 (m, 2H, Ar*H^3*). IR: ν = 2981.0 (w), 2928.6 (w), 1729.7 (s; acetate C=O), 1530.4 (w; Boc C=O), 1433.0 (w), 1369.3 (m), 1226.8 (s; acetate C-O), 1117.9 (w), 1019.7 (s, acetate C-O), 944.1 (w), 796.9 (w), 604.17 (w).

Boc deprotection of polymer to yield "H-PVAc-NH$_2$" (6)

The boc-protected polymer **5** was dissolved in the DCM component of 3:1 DCM:TFA such that the concentration of the boc-group was of the order of 10^{-7} mol mL^{-1}. The TFA was added and the solution was then stirred at room temperature for one hour. After this time, ice was added and the mixture transferred to a large flask. Sodium hydrogen carbonate was added until the effervescence ceased. The biphasic-mixture was separated and the organic layer washed with water. After drying with sodium sulphate and filtration, solvent was removed under vacuum to give a material of similar physical character to the parent polymer which was purified using precipitation from THF into petrol (40-60 °C fraction, >99%). ^{1}H NMR (CDCl$_3$), (400 MHz): δ_H = 1.60 - 1.96 (m, 2nH, C*H$_2$*CH (backbone)), 1.97-2.10 (t, 3nH, (C*H$_3$*), 2.49 (br, 2H, ArC*H$_2$*), 4.10 (m, 2H, C*H$_2$*C(OAc)*H$_2$*), 4.77-5.30 (br m, n-1H, C*H$_2$*CH (backbone)), 6.61 (d, ^{3}J$_{HH}$ 8.0 Hz, 2H, Ar*H^2*), 6.94 (m, 2H, Ar*H^3*). IR: ν = 2982.8 (w), 2929.7 (w), 1729.7 (s; acetate C=O), 1432.8 (w), 1369.7 (m), 1227.2 (s; acetate C-O), 1119.1 (w), 1019.9 (s, acetate C-O), 944.0 (w), 797.6 (w), 604.3 (w).

Azidation of aniline terminated polymer to yield "H-PVAc-N₃" (7)

Polymer **6** (1.0 eq. of amine) was dissolved in 9:1 (v/v) AcOH:water (25 mL). The solution was cooled in an ice bath and sodium nitrite (1.5 eq) was added. After ten minutes, sodium azide (2.0 eq.) was added and stirring continued for 1 h. After this time, DCM (10 mL) was added. The organic layer was separated and the aqueous layer washed with further DCM (3 x 10 mL). The combined organic fractions were then washed with water (3 x 50 mL), dried over sodium sulphate and evaporated to dryness to give polymer **7** (>99%) which was used without further purification. ^{1}H NMR (CDCl₃), (400 MHz): δ_H = 1.59-1.95 (m, 2nH, CH_2CH (backbone)), 1.97-2.10 (t, 3nH, (CH_3), 2.58 (br, 2H, ArCH_2), 4.11 (t, 2H, CH_2C(OAc)H_2), 4.77-5.30 (br m, (n-1)H, CH_2CH (backbone)), 6.94 (d, $^3J_{HH}$ 8.4 Hz, 2H, ArH^2), 7.14 (d, $^3J_{HH}$ 8.4 Hz 2H, ArH^3). IR: v = 2981.0 (w), 2929.8 (w), 2115.2 (w; azide), 1730.2 (s; acetate C=O), 1432.5 (w), 1370.1 (m), 1227.4 (s; acetate C-O), 1118.0 (w), 1020.0 (s, acetate C-O), 944.4 (w), 797.2 (w), 603.7 (w).

Alkylation of aniline terminated polymer to yield "H-PVAc-Br" (8)

Polymer **6** (1.0 eq. of amine) was dissolved in dry DCM (50 mL) under nitrogen with stirring. The solution was cooled to 0 °C in an ice bath and bromoacetyl bromide (2.0 eq.) was added. The ice bath was removed and the solution stirred for 1 h. The residue was purified using precipitation from THF into petrol (40-60 °C fraction) to give the dark brown polymer **8** (>99%). ^{1}H NMR (CDCl₃), (400 MHz): δ_H = 1.62-1.96 (m, 2nH, CH_2CH (backbone)), 1.97-2.10 (t, 3nH, (CH_3), 2.57 (br, 2H, ArCH_2), 3.71 (s, 2H, BrCH_2), 3.97 (s, 2H, CH_2C(OAc)H_2), 4.73-5.21 (br m, n-1H, CH_2CH (backbone)), 7.11 (d, $^3J_{HH}$ 7.2 Hz, 2H, ArH^2), 7.41 (d, $^3J_{HH}$ 7.2 Hz 2H, ArH^3), 8.23 (s. 1H, NH).

Purification of SWCNTs

A bulk solution of sodium naphthalide (NaNp) in (DMAc) was prepared by stirring sodium (50 mg) and naphthalene (278 mg) in DMAc (50 mL) using a glass stirrer bar. This solution was used within a week of preparation. SWCNTs (100 mg) were dried under vacuum ($\sim 10^{-2}$ mbar) at 300 ^{o}C for 1 h and 16 h at room temperature before leaving to soak for 24 h in 9.6 mL of NaNp solution diluted with 80.4 mL of DMAc. The mixture was centrifuged at 10,000 *g* for 30 min and the supernatant containing dissolved amorphous carbon, catalyst particles, and short/defecting SWCNTs was discarded. The remaining SWCNTs were left in an atmosphere of dry oxygen overnight before washing with copious acetone, then copious DI water to leave purified SWCNTs (*ca.* 80 % initial weight). Procedure adapted from *Clancy et al.*[22]

General Procedure for diazonium grafting

Procedure adapted from Chadwick *et al.*[21] Purified SWCNTs (5 mg) were added to dry DMF (50 mL) and bath sonicated for 30 min. After this time, PVAc-NH$_2$ (200 mg) was added and the mixture heated at 70 °C. Upon reaching this temperature, isoamyl nitrite (0.1 mL) was added. The suspension was then stirred for 18 h, then allowed to cool slightly before filtering through a 100 nm PTFE membrane. Before drying on the filter membrane, the membrane was placed in a further 100 mL of DMAc and briefly sonicated to redisperse the nanotubes. The resulting suspension was again filtered through a fresh membrane. The resulting nanotube filtrate was washed with THF (100 mL) and dried under vacuum. The procedure was repeated without the addition of polymer solution to give the 'diazonium control'.

General procedure for azide grafting

Purified SWCNTs (5 mg) were added to dry DMAc (50 mL) and bath sonicated for 30 min. Polymer **7** (200 mg) was added and the mixture heated at 140 °C with stirring for three days. After this time, the suspension was allowed to cool slightly before being filtered through a 100 nm PTFE membrane. Before drying on the filter membrane, the membrane was placed in a further 100 mL of DMAc and briefly sonicated to redisperse the nanotubes. The resulting suspension was again filtered through a fresh membrane. The resulting nanotube filtrate was washed with THF (100 mL) and dried under vacuum. Procedure adapted from Qin *et al.*[23] The procedure was repeated without the addition of polymer to give the 'azide control', and was repeated using polymers **4** and **6** (M_w 5767) as non-grafting polymer controls.
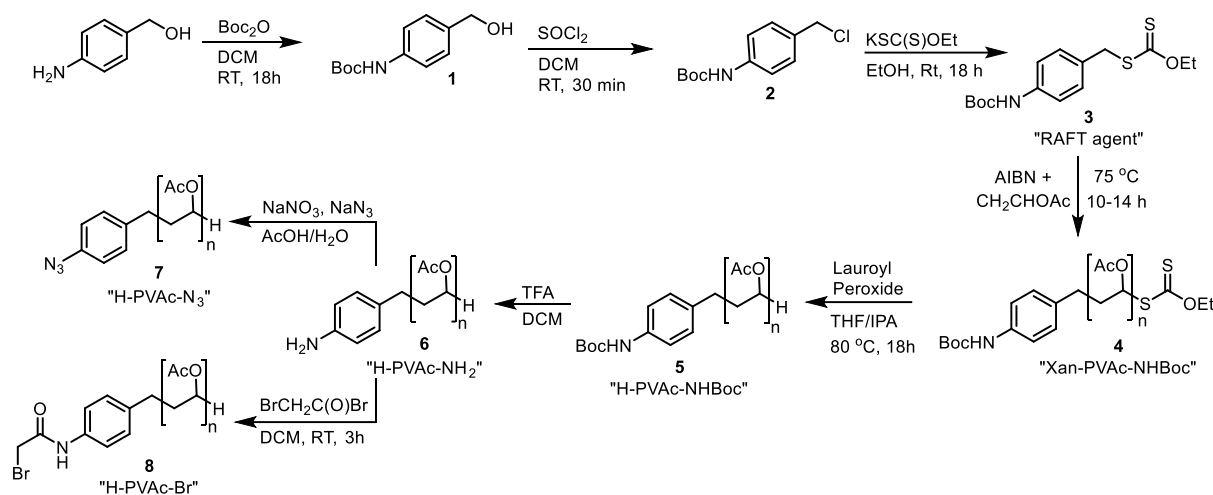
General Procedure for nanotubide grafting

Procedure adapted from Clancy *et al.*[24]. Purified SWCNTs (12 mg) were dried under vacuum ($\sim 10^{-2}$ mbar) at 300 °C for 1 h and at room temperature for 16 h. In a nitrogen glovebox, the SWCNTs were stirred in NaNp/DMAc solution (24 mL, 1 mmol Na, for preparation see SWCNT purification) for 24 h. After this time, the solution was diluted with sufficient DMAc to afford a final 0.1 mg mL^{-1} solution, taking into account the additional DMAc that would be added with the polymer. A solution of polymer **8** (0.33 mmol) in DMAc was added (2.5 mM) and the solution stirred overnight. The solution was removed from the glovebox residual charge was removed by bubbling dry oxygen through the dispersion for 15 min before being filtered through a PTFE filter membrane. Before drying on the filter membrane, the membrane was placed in a further 100 mL of DMAc and briefly sonicated to redisperse the nanotubes. The resulting suspension was again filtered through a fresh membrane. The resulting nanotube filtrate was washed with THF (100 mL) and dried under vacuum. The procedure was repeated without the addition of polymer solution to give the 'nanotubide control'.

Dispersibility measurements

SWCNTs (2.0 mg carbon framework, *e.g.* 3 mg of functionalised SWCNTs with 50% grafting ratio) were placed in a glass vial and DMAc (4.0 mL) was added; the total weight of functionalised material added was calculated using grafting density derived from TGA, to ensure a consistent weight of SWCNT framework. The sample was bath sonicated for 30 min, the suspension transferred to a centrifuge tube and centrifuged at 20,000 *g* for 30 min. A portion of the decanted supernatant (0.4 mL) was taken and diluted with further DMAc (0.8 mL). UV-vis spectra were recorded between 300 – 1200 nm and measurements were repeated three times. Dispersibilities were calculated using the absorbance recorded at 660 nm (less the measurement for neat DMAc) using an extinction coefficient of 3616.6 mL mg^{-1} m^{-1} ($\pm$ 7.4 %, ESI Table S2).

3. Results and Discussion

Asymmetric end group controlled polymers were prepared via reversible addition-fragmentation chain transfer (RAFT); mono-para-aniline and hydrogen were selected as the end groups, since the primary amine facilitates all the chosen grafting strategies, allowing the same series of polymers to be compared. Polyvinyl acetate (PVAc) was selected as a well-studied RAFT-synthesised polymer, highly soluble in the solvent used throughout this work (DMAc) while remaining unreactive towards all the chemistries employed. In addition, PVAc is the typical intermediate in polyvinyl alcohol synthesis, which has been used as the matrix for some of the highest performance SWCNT composites to date,[25] providing a potential future application for the synthesised f-SWCNTs.

Scheme 1. Preparation of RAFT agent **3**, Polymerisation of vinyl acetate, and subsequent end-group modifications.

The preparation of the RAFT reagent (Scheme 1) was adapted from Tong *et al.,*[26] with *O*-ethyl xanthate used *in lieu* of *O*-2-methoxyethyl xanthate, for reasons of availability. The RAFT agent (**3**) was synthesized from 4-aminobenzalcohol through tert-butyloxycarbonyl (Boc) protection of the amine, followed by chlorination of the alcohol with thionyl chloride to form the benzyl chloride (**2**) before final substitution with *O*-ethyl xanthate to give **3**. Vinyl acetate was polymerised from **3** using 60 equivalents of monomer under typical RAFT conditions[27] (75 °C, Ar atmosphere, solvent free). Most polymers were characterised using gel permeation chromatography (GPC), however for oligomers of less than 1000 Da, ^{1}H NMR end-group analysis was used; for products where both GPC and NMR was possible, number average molecular weights derived from NMR analysis correlated with the values obtained with GPC (ESI Table S1). Molecular weight was monitored as a function of time for 60 eq. monomer versus **3** (Fig. 1a): the reaction required an approximately 10 hour RAFT initiation period,[28] after which, the M_w increased rapidly until a plateau was seen at a weight corresponding to approximately 120 equivalents. The low efficiency of the RAFT agent (*ca.* 50%) may be attributed to premature termination due to dimerization of the carboradical (here

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CH$_2$PhNHBoc) during the initiation stage.[28] The specific kinetics of this particular polymerization system was not investigated further, however, and polymers of predetermined molecular weight were created through stoichiometric monomer control, taking into account the RAFT agent efficiency. Polymers were purified through precipitation into petroleum ether, removing short chains and side products, with recovery typically >90% (by weight), and final PDIs ranging between 1.10–1.17 (ESI, Table S1).
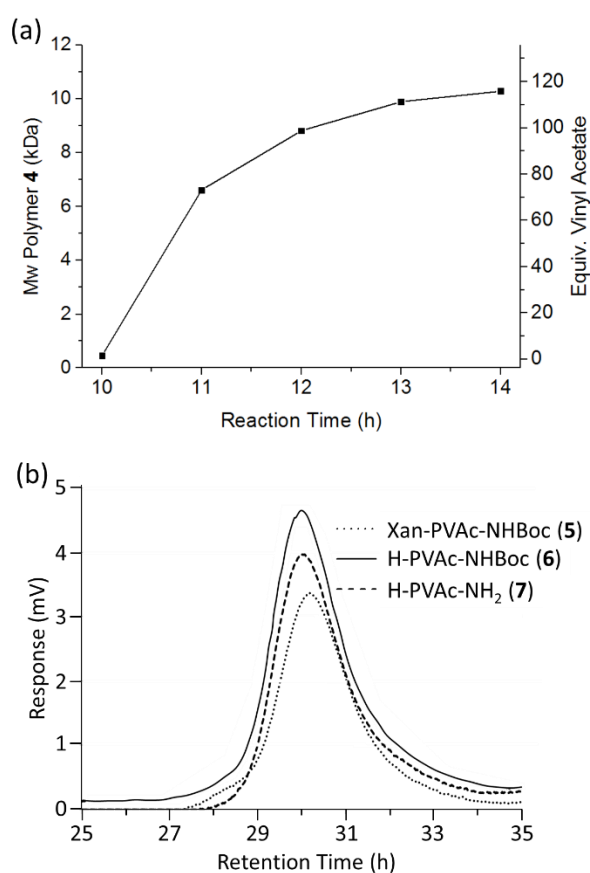

Figure 1. (a) PVAc M$_w$ measured via GPC as a function of time for 60:1 initial ratio of vinyl acetate to RAFT agent, (b) GPC curves of as-polymerised and end-group modified PVAcs.

Subsequent end-group functionalisations were performed to facilitate the grafting reactions (Scheme 2); reactions were performed on the same batch of polymer to ensure

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molecular weight and PDI consistency. After polymerization, the xanthate was cleaved using lauryl peroxide[29] to give the hydrogen-terminated H-PVAc-NHBoc (**5**), with NMR showing elimination of the xanthate *O*-ethyl protons ($\delta = 4.65$, Fig. 2) and emergence of a peak corresponding to the terminal hydrogens ($\delta = 4.09$). Subsequently, the polymers' aniline Boc protection was removed through addition of trifluoroacetic acid, exposing the amine used to adhere all grafting functionalities, giving H-PVAc-NH$_2$ (**6**). Removal of the Boc group could be seen through disappearance of the Boc carbonyl in IR spectroscopy (1530.4 cm^{-1}, ESI Fig. S2) and a substantial downshift in the aryl peaks in NMR (Fig. 2). The post-polymerisation end-group manipulations were shown to not influence the polymer molecular weight of the backbone chain with GPC showing a single peak with no broadening before and after all steps (Fig. 1b).
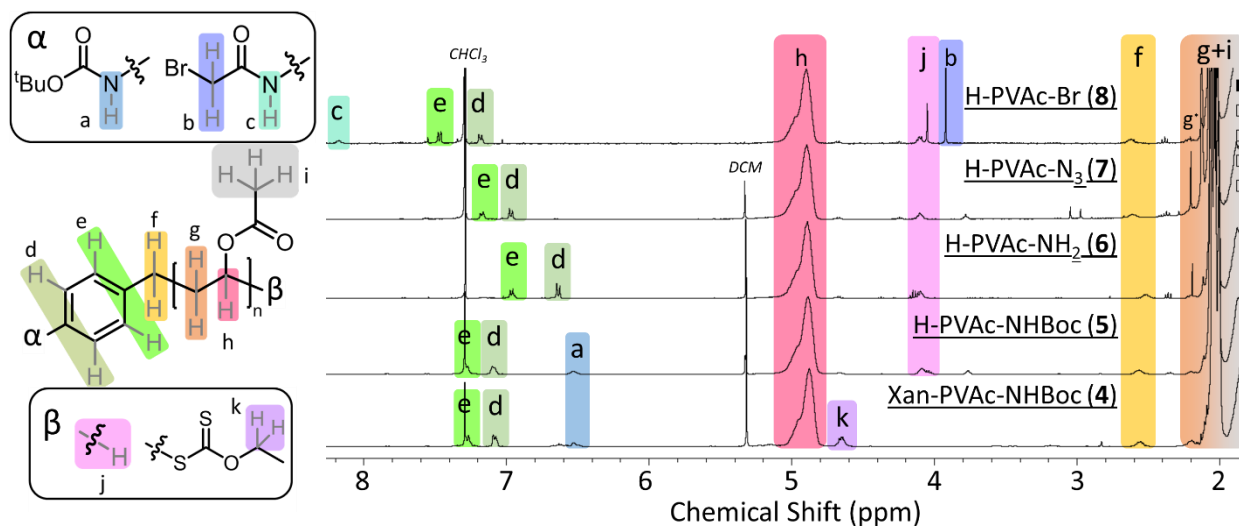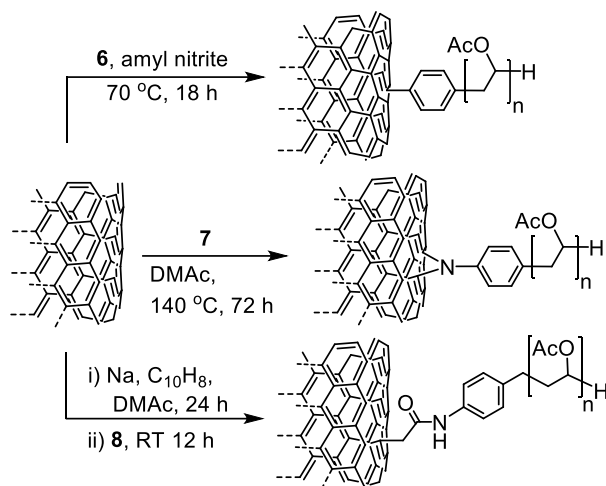

Figure 2. ^{1}H NMR spectra of PVAc with varying end groups. g* at $\delta \sim 2.2$ ppm corresponds to "g" assignment closest to the aryl (*i.e.* $C_6H_4CH_2CH_2$). The $\delta < 2$ ppm region (containing backbone hydrogens g/i) is excluded here for clarity: full spectra are provided in the ESI (Fig. S3–S13), and full values and assignment given in experimental section

The azide-terminated polymer (**7**) was synthesised by ipso-substitution of azide via an *in situ* generated diazonium at the aniline using typical azidination conditions.[30] Substitution was confirmed through appearance of the characteristic asymmetric azide stretch in IR (2115.2 cm^{-1}); the reaction was quantitative as illustrated by the disappearance of the aryl aniline peaks in ^{1}H NMR (Fig. 2). Bromination to H-PVAc-Br (**8**) was performed through reaction with bromoacyl bromide and was confirmed by the appearance of a singlet in NMR corresponding to the acetyl endgroup (4.04 ppm) and a highly upshifted amide hydrogen (8.18 ppm). Acyl halides were required for amidification, as 'milder' condensation reactions would lead to partial deacetylation of the PVAc backbone. It is also noted that the use of acyl chlorides led to an equilibrium between chlorine and bromine terminated polymers due to attack of the liberated chloride anion; the use of the acyl bromide bypassed this issue. Characteristic acetate ester peaks remained constant at approximately 1730, 1227 and 1020 cm^{-1} for **6**, **7**, and **8**, indicating stability of the acetate backbone throughout the transformations. Diazonium-terminated polymers were generated *in situ* from **7** during the grafting to SWCNTs, following an established procedure,[21] and not isolated for characterization.

"The modified PVAc (**6**, **7** and **8**) were grafted to the SWCNTs (Scheme 2) using reaction conditions adapted from literature.[21, 23, 24] Briefly, diazonium reactions were performed by adding **6** to a sonicated dispersion of SWCNTs at 70 °C and forming the diazonium *in situ* with isoamyl nitrite and heating for 18h. Azide functionalisation was performed by adding **7** to a sonicated dispersion of SWCNTs in DMF and heating at 140 °C for 72 h. Bromide functionalisation was performed by stirring **8** and nanotubide DMAc solution at RT for 24 h in a nitrogen glovebox. Nanotube and polymer quantities and concentrations were kept constant between reactions. The f-SWCNTs in all cases were filtered, washed with copious DMAc and THF, before redispersing and refiltering to remove excess polymer. To explore the effects of

these reaction environments, the SWCNTs were subjected to identical conditions and work-up, without the addition of the polymer, to generate "polymer-free control samples".

Scheme 1. PVAc functionalisations of SWCNTs.

In TGA, all polymer-free controls show modest additional weight losses between 100–700 °C (ESI Fig. S14), indicative of either physisorption or adventitious functionalisation by the reaction medium. The small weight loss from the bromide polymer-free control (GR = 5.2 %) is thought to derive from the introduction of oxygen-containing groups during discharge, as has been previously reported.[31] Both diazonium and azide polymer-free controls involve heating in DMF, leading to some apparent functionalization due to degradation of DMF which proceeds via radical intermediates[32] which are likely to react with the SWCNT framework. The diazonium control exhibits a low grafting ratio (2.5%), particularly in comparison to the azide polymer-free control (8.3%), in line with the difference in reaction temperatures (70 and 140°C, respectively). Similarly, while the dispersibilities of the diazonium (18.4 μg mL^{-1}) and nanotubide (3.0 μg mL^{-1}) controls remain similar to untreated SWCNTs (11.7 μg mL^{-1}), the dispersibility of the azide control increases notably (57.8 μg mL^{-1}), as has been seen previously for sonochemically degraded amidic solvents adsorbed on SWCNTs.[33]

Nominally unreactive polymers **4** (as-polymerised Xan-PVAc-NHBoc) and **6** (fully deprotected H-PVAc-NH$_2$, both M$_n$ ~5731) were subjected to the azide grafting conditions (the most extreme conditions) as controls to explore potential polymer wrapping/adsorption on the SWCNTs. The grafting ratios of each (6.3 % and 8.2 % respectively) were similar to the azide polymer-free control; however, the thermogravimetric data (ESI Fig. S14) showed a steep increase in degradation at *ca.* 300 °C, typical of both commercial and synthesized PVAc (ESI Fig. S1); no equivalent continuous decrease was seen for the previous polymer-free controls, suggesting that the weight loss relates to residual polymer rather than adsorbed degraded solvent. The dispersibility of the **4** and **6** control SWCNTs only increased mildly (28.8 and 31.7 µg mL^{-1} respectively). It seems that the free polymer occludes the SWCNT surface and reduces the trapping of degraded solvent.
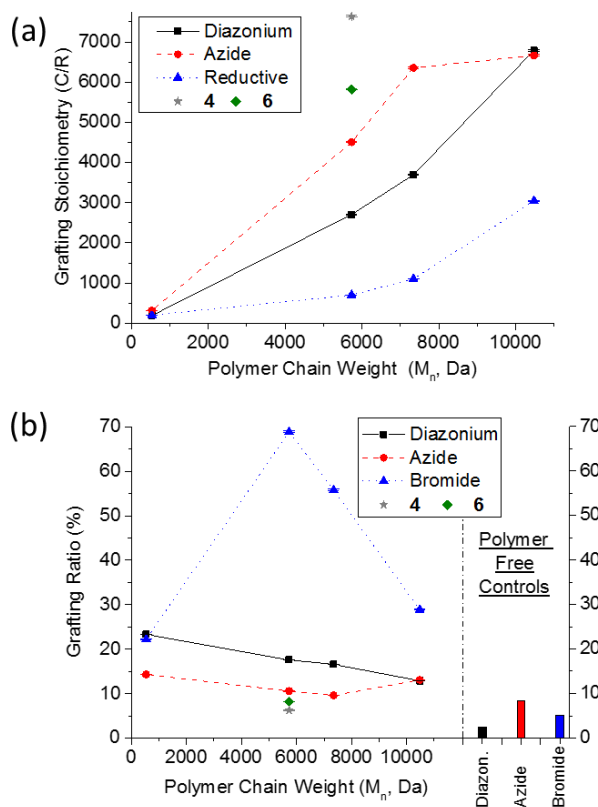
Figure 3. (a) Grafting stoichiometry of f-SWCNTs as a function of PVAc backbone molecular weight for diazonium (black square, solid line), azide (red circle, dashed line) and reductive (blue triangle, dotted line) routes and non-grafting polymers **4** (grey star) and **6** (green diamond) under azide grafting conditions. (b) Grafting ratio of f-SWCNTs. Controls of SWCNTs under the respective functionalization conditions, in the absence of polymer, are given in bar chart on the right.
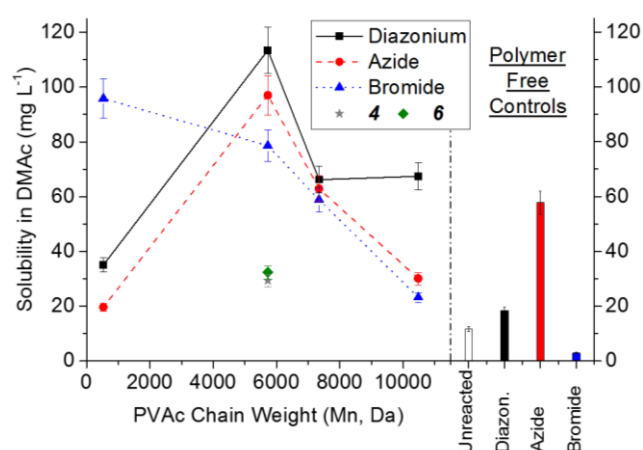

Figure 4. Dispersibility of f-SWCNTs in DMAc (after initial dispersion at 500 mg L^{-1} and centrifugation) versus PVAc backbone weight for diazonium (black square, solid line), azide (red circle, dashed line), and reductive (blue triangle, dotted line) functionalisation routes, and non-grafting polymers **4** (grey star) and **6** (green diamond) under azide grafting conditions. Controls of SWCNTs under the respective functionalization conditions in the absence of polymer given in bar chart on the right.

Grafted f-SWCNTs in all reaction routes also show polymer-like thermogravimetric behavior, indicating that weight loss is attributable to PVAc. There is a clear trend in grafting ratio (Fig. 3) between reaction types: bromide functionalisation shows the highest degree of functionalisation, followed by diazonium, with azide showing the lowest grafting ratio. The high degree of grafting seen for the bromide reaction is likely due to the higher degree of

individualization (thus larger accessible SWCNT surface for functionalisation) intrinsic to solutions of reduced SWCNTs; the sonication derived dispersions used for the azide and diazonium reactions are likely to remain significantly bundled. For all the reaction types, increasing molecular weight decreases grafting density (Fig. 3a), as expected, due to steric occlusion of the accessible SWCNT surface.[24] Generally, the grafting ratio decreases with increasing molecular weight (Fig. 3b), independent of grafting route, as seen in previous research.[21] In the case of the bromide route, the shortest, oligomer chain (M_n 600 Da), however, does not have as high a grafting ratio as might be expected from steric interactions alone. This sample has the lowest C/R ratio (200), and hence highest consumption of charge, and it is possible that the reaction is limited by availability of electrons on the SWCNTs. The reactivity of nanotubide is complex, thought to be governed by the reduction potential of the electrons, which is a function of the degree of charging, due to the continuum density of states. As the charge is consumed, the Fermi level of the nanotubide falls, eventually below the level needed for reaction.[18, 31, 34]

Significant covalent functionalisation can be seen for the bromide and diazonium routes with the grafting ratios clearly exceeding all controls (by at least a factor of two). On the other hand, the grafting ratios of azide grafting reactions are of the same order as the non-grafting polymer controls. Nevertheless, the high dispersibility of azide grafted materials compared to non-grafting controls (118.1 µg mL^{-1} vs < 32 µg mL^{-1}) indicates a different structure, and suggests some grafting. For all the covalent grafting routes, the best dispersibilities were greater than the polymer-free and unreactive polymer control samples, highlighting the importance and utility of covalent grafting. The f-SWCNT dispersibility showed a strong correlation with the molecular weight of the initial polymer, reaching the maximum at a M_w of ~5 kDa for both diazonium and azide reactions (the bromide functionalised sample showed high dispersibility

at both 5 kDa and for the oligomer system). Given the differences in grafting ratios between grafting methodologies for polymers of matching polymer size, these results confirms that the dispersibility of the f-SWCNTs is dominated by polymer molecular weight and not grafting ratio/stoichiometry.

Conclusions

In summary, three routes to SWCNT polymer *graft-to* functionalization were successfully compared through the use of a bespoke low-PDI, monoterminal-amine PVAc: simple end-group transformations provided equivalent length polymer chains suitable for comparing azide, diazonium, and bromide *graft-to* reactions. Bromide functionalisation through the use of reduced SWCNTs provides the highest grafting ratios; the difference in grafting ratios between reaction types highlights that degree of fuctionalisation in *graft-to* reactions are not controlled solely by polymer size. The success of bromide functionalization here is attributed to the maximized accessible SWCNT surface area from the spontaneously individualized anionic nanotubes. The bromide functionalisation gives the best grafting ratios but requires more stringent inert conditions and is less versatile; many solvents and potential side groups may react with the charged nanotubide framework. Of the other methodologies, diazonium grafting generally gives higher grafting ratios, and higher dispersibility than azide functionalisation, while requiring milder conditions (avoiding contaminating solvent degradation products) and shorter reaction times.

In terms of polymer molecular weight, shorter polymers generally maximize grafting ratio, as they minimize steric repulsion between the grafted polymer coils, but the best dispersibilities are found at intermediate polymer molecular weights, around 5 kDa. Crucially, the dispersibilities of the f-SWCNTs were shown to be most closely linked to the initial polymer's

molecular weight, and not the grafting methodology, or total weight of grafted polymer. Overall, the bromide route is recommended (where compatible) to maximise the degree of functionalisation, while diazonium grafting can be used in other scenarios. Polymer functionalization of SWCNTs is relevant to wide range of applications, particularly in nanocomposites; strategies to maximize the grafting ratio and dispersibility should offer significant benefits. Many of trends observed in this study are likely to be applicable to other nanocarbons which are known to react in similar conditions,[6] allowing the processing of a broad range of nanomaterials to be improved.

Acknowledgements

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