Synthesis of Hydrophobic and Hydrophilic Graphitic Carbon Nanofiber Polymer Brushes

Lang Li and Charles M. Lukehart*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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Herringbone graphitic carbon nanofiber (GCNF)−polymer brushes are prepared by atom transfer radical polymerization (ATRP) using the "grafted-from" synthesis strategy. Polymerization of acrylate esters occurs at surface sites covalently derivatized with ATRP initiators to form GCNF−poly(*n*-butyl acrylate), GCNF−poly(isobutyl methacrylate), and GCNF−poly(*tert*-butyl acrylate) polymer brushes. Acid hydrolysis of the GCNF−poly(*tert*-butyl acrylate) polymer brush gives a GCNF−poly(acrylic acid) polymer brush. Solution dispersibilities of GCNF−polymer brushes are controlled by the solubility properties of the polymer brush component, with GCNF−poly(acrylate ester) brushes being hydrophobic, whereas the GCNF−poly(acrylic acid) brush is hydrophilic. Because of the unique atomic structure of GCNFs, a high surface density (ca. 3 chains/10 nm^2 of GCNF surface) of polymer brush functionalization is realized.

Introduction

Interest in developing carbon nanostructures appropriately surface-derivatized for diverse applications remains high. Considerable progress has been made in controlling the dispersibility and wettability properties of single-walled (SWNTs) or multiwalled (MWNTs) carbon nanotubes through either covalent or noncovalent surface derivatization.[1−3] Most recently, radical initiator functional groups appropriate for effecting in situ atom transfer radical polymerization (ATRP) have been grafted to surface sites on SWNTs or MWNTs to form SWNT−poly(*n*-butyl methacrylate), SWNT−polystyrene, SWNT−poly(methyl methacrylate), SWNT−poly(*tert*-butyl acrylate), SWNT−poly(acrylic acid), MWNT−poly(methyl methacrylate), and MWNT−poly(methyl methacrylate)$_x$ (hydroxyethyl methacrylate)$_y$ as polymer brushes having either hydrophobic or hydrophilic surfaces.[4−7] ATRP methods have also been used to extend polymer chains within carbon nanotube−polymer brushes.[8,9]

Graphitic carbon nanofibers (GCNFs) represent a class of nanostructured carbon fibers with atomic structures uniquely different from that of carbon nanotubes.[10] Herringbone GCNFs possess canted graphene sheets (also described as geodesic-like conical graphene sheets) stacked in a nested fashion along the long fiber axis. GCNFs of this type can be prepared with average diameters of 25−200 nm and lengths on the micrometer scale. The graphitic atomic structure of herringbone GCNFs gives a carbon nanofiber long-axis surface comprising C(sp^2) edge sites, usually passivated by hydrogen atoms.

Surface functionalization of herringbone GCNFs with reactive linker molecules using surface oxidation and carboxyl-group-coupling chemistry occurs without degradation of the structural integrity of the GCNF backbone, and affords surface-derivatized GCNFs with a high surface density of functional groups.[11] Covalent binding of such linker molecules to either polymer resins or ceramic condensation oligomers gives GCNF−polymer or GCNF−ceramer hybrid materials.[11−13] An even greater complexity of functional group derivatization could be achieved by grafting organic polymers to GCNF surface sites to give GCNF−polymer brushes with tunable dispersibilities and surface reactivity.

We now report the synthesis of herringbone GCNF−poly(*n*-butyl acrylate) (GCNF−PBA), GCNF−poly(isobutyl methacrylate) (GCNF−PiBMA), GCNF−poly(*tert*-butyl acrylate) (GCNF−P*t*BA), and GCNF−poly(acrylic acid) (GCNF−PAA) polymer brushes. These materials have been prepared by ATRP using a "grafted-from" approach in which a radical initiator, such as (4-hydroxymethyl)benzyl-2-bromopropionate (HBBP) or 2-hydroxyethyl-2′-bromopropionate (HEBP),

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* To whom correspondence should be addressed. Email address: chuck.lukehart@vanderbilt.edu.

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is covalently coupled to surface carboxylic acid sites of oxidized GCNFs, GCNF−CO$_2$H.[14] Whereas GCNF−poly(acrylate ester) polymer brushes exhibit hydrophobic dispersibility, the GCNF−PAA brush is hydrophilic. A synthesis strategy amenable to the preparation of a wide variety of GCNF−polymer materials is demonstrated.

Experimental Section

Experimental Methods and Procedures. Gaseous ethylene, hydrogen, and helium were procured from Air Liquide Gas. 1,4-Benzenedimethanol (97%), ethylene glycol (99.8%), 2-bromopropionyl bromide (97%), methyl 2-bromopropionate (MBrP, 98%), CuBr (99.999%), CuCl (99.999%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%), 4-(dimethylamino)pyridine (DMAP, 99%), and triethylamine (TEA, 99.5%) were purchased from Aldrich, and were used as received. *n*-Butyl acrylate (BA, Aldrich, 99%), isobutyl methacrylate (iBMA, Aldrich, 99%), and *tert*-butyl acrylate (*t*BA, Aldrich, 98%) were purified by being passed through an alumina column, and were stored under N$_2$ at −15 °C. Solvents were distilled before use, and other reagents were used without further purification.

Transmission electron microscopy (TEM) was performed on a Philips CM-20T electron microscope operating at 200 keV. ^{1}H NMR spectra at 300 MHz were recorded on a Bruker AC300 Fourier transform spectrometer, using CDCl$_3$ as a solvent. Infrared spectra (IR) were obtained from KBr pressed pellets with an ATI Mattson Genesis series FT-IR spectrometer. Thermogravimetric analyses (TGA) were performed on a Thermal Analysis Instruments high-resolution TGA 2950 thermogravimetric analyzer. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA. BET surface-area analysis was carried out on a NOVA 1000 high-speed surface area & pore size analyzer with nitrogen gas as the absorbent. Atomic force microscopy (AFM) images were taken with a Digital Instruments multimode IIIa nanoscope SPM in the tapping mode. Polymer molecular weights and polydispersity measurements, obtained by GPC-MALLS analysis, were provided by Dr. R. Cueto, Biodynamics Institute, Louisiana State University, Baton Rouge, LA.

Synthesis of (4-Hydroxymethyl)benzyl-2-bromopropionate (HBBP). A 500 mL round-bottomed flask was charged with 13.06 g (94.5 mmol) of 1,4-benzenedimethanol, 20 mL (0.145 mol) of TEA, 0.24 g (2.0 mmol) of DMAP, and 200 mL of anhydrous THF. The solution was cooled to 0 °C, and a solution of 10 mL (94.5 mmol) of 2-bromopropionyl bromide dissolved in 20 mL of anhydrous THF was added dropwise under nitrogen at 0 °C over 2 h. The reaction mixture temperature was then raised to 40 °C, and the mixture was stirred for 24 h. Solids were removed by suction filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in 100 mL of deionized water, and was extracted with CH$_2$Cl$_2$ three times. The organic phase was dried over MgSO$_4$ overnight, and the solvent was removed by rotary evaporation. The light yellow liquid product of HBBP was obtained in a yield of 69.5%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.90 (CH(***CH***$_3$)Br), 5.22 (***CH***$_2$-OCO), 4.73 (HO-***CH***$_2$), 4.40 (***CH***(CH$_3$)Br), 2.06 (***HO***-CH$_2$), 7.40 (CH$_2$-***C***$_6$H$_4$-CH$_2$). Anal. Calcd (wt %) for C$_{11}$H$_{13}$O$_3$Br: C, 48.35; H, 4.76; O, 17.59; Br, 29.30. Found: C, 48.39; H, 4.68; O, 17.42; Br, 29.51.

Synthesis of 2-Hydroxyethyl-2′-bromopropionate (HEBP).[4] A 500 mL round-bottomed flask was charged with 62.0 g (1.00 mol) of ethylene glycol, 16.0 mL (0.114 mol) of TEA, and 200 mL of anhydrous THF. The solution was cooled to 0 °C, and a solution of 21.6 g (0.10mol) of 2-bromopropionyl bromide dissolved in 20 mL of anhydrous THF was added dropwise under nitrogen at 0 °C for 2 h. The reaction temperature was then raised to 40 °C for 24 h. Solids were removed by suction filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in 100 mL of deionized water, and was extracted with CH$_2$Cl$_2$ three times. The organic phase was dried over MgSO$_4$ overnight, and the solvent was removed by rotary evaporation. The colorless liquid product was collected by distillation under reduced pressure and was obtained in 61.8% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.90 (CH(***CH***$_3$)Br), 4.29 (***CH***$_2$−OCO), 3.85 (HO-***CH***$_2$), 4.53 (***CH***(CH$_3$)Br), 2.06 (***HO***-CH$_2$).

Synthesis of Herringbone GCNFs. GCNFs of herringbone structure were grown from an Fe/Cu growth-catalyst powder as reported elsewhere.[15] The Fe/Cu catalyst with an atomic ratio of 7:3 was prepared by coprecipitation of Fe(NO$_3$)$_3$•9H$_2$O and Cu(NO$_3$)$_2$•3H$_2$O with ammonium bicarbonate in water. The precipitate was dried at 110 °C overnight, and was ground to a fine powder. The powder was weighed into a quartz boat, placed in a tube furnace, and calcined in an air flow at 400 °C for 4 h. A H$_2$/He (1:4) flow of 250 mL/min was then applied to reduce the iron/copper oxide at 500 °C for 20 h. After further reduction of the catalyst at 600 °C for 2 h, ethylene was introduced to grow the GCNFs with the gas composition of C$_2$H$_4$/H$_2$/He (4:1:1) at 600 °C over 90 min. The GCNFs were cooled to room temperature under He protection.

Oxidation and Acylation of GCNFs. Surface oxidization of as-prepared GCNFs was performed by heating as-prepared GCNFs in concentrated nitric acid at 140 °C for 4 h. The product was filtered and washed with deionized water until pH $\approx$ 7. The surface-oxidized carbon nanofibers (GCNF−CO$_2$H) were dried in vacuo at room temperature for 2 days to remove residual water. The GCNF−CO$_2$H nanofibers were then acylchlorinated by reaction with thionyl chloride at 70 °C for 24 h in the presence of a small amount of dimethylformamide (DMF). The mixture was cooled, and was washed with anhydrous THF under nitrogen until the supernatant was clear. The black solid GCNF−C(O)Cl product was dried under a nitrogen flow at room temperature before further reaction.

Preparation of HBBP-Immobilized GCNFs (GCNF−HBBP−Br). A 100 mL round-bottomed flask was charged with 0.42 g of GCNF−C(O)Cl, 8.47 g (31.1 mmol) of HBBP, and 0.03 g (0.29 mmol) of TEA. The mixture was allowed to react at 75 °C under the protection of N$_2$ for 144 h. The black solid was washed with methanol several times to remove excess HBBP and TEA. The product was collected by filtration through a 0.2 μm Millipore nylon membrane, and was dried in a vacuum. Elemental analysis (wt %): C, 90.64; H, 0.74; O, 6.09; Br, 0.92.

Preparation of HEBP-Immobilized GCNFs (GCNF−HEBP−Br). A 100 mL round-bottomed flask was charged with 0.98 g of GCNF−C(O)Cl, 6.53 g of HEBP, and 0.047 g of TEA. The mixture was allowed to react at 75 °C under the protection of N$_2$ for 96 h. The black solid was washed with methanol several times to remove excess HEBP and TEA. The product was collected by filtration through a 0.2 μm Millipore nylon membrane, and was dried in a vacuum. Elemental analysis (wt %): C, 92.89; H, 0.45; O, 5.98; N, 0.18; Br, 0.50.

Synthesis of GCNF−Poly(*n*-butyl acrylate) (GCNF−PBA). For a typical polymerization, a 100 mL dried Schlenk flask was charged with 200 mg of GCNF−HBBP−Br, 112 mg (0.78 mmol) of CuBr, 162 μL (0.78 mmol) of PMDETA, and 1.00 g (7.8 mmol) of *n*-butyl acrylate. The reaction mixture was degassed by five

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Table 1. Conditions and Results of ATRP of *n*BA Initiated by HBBP[a]

sample	catalyst ratio[b]	*t* (h)	M_n	M_w/M_n	yield (%)
PBA0	50:1:1:1	2	5300	1.20	99.1
PBA1[c]	50:1:1:1	2	4900	1.49	58.5
PBA2[d]	50:1:1:1	20	7300	1.31	98.6

[a] A reaction temperature of 70 °C was used. [b] Catalyst ratio = [*n*BA]:[CuBr]:[PMDETA]:[HBBP]. [c] In the presence of as-prepared GCNFs, [BA]:[GCNFs] = 10:1 (w/w). [d] In the presence of GCNF−CO_2H, [BA]:[GCNF−CO_2H] = 10:1 (w/w).

freeze−pump−thaw cycles. The flask was put into a 70 °C oil bath, and the mixture was stirred for 116 h. The reaction was quenched by liquid nitrogen, and 30 mL of THF was added to disperse the black solid. The product was filtered through a 0.2 μm Millipore nylon membrane, and was washed with THF. The dispersion−filtration−wash process was repeated six times to ensure that no ungrafted polymers remained in the residue. The dark solid was then dispersed in methanol followed by filtration to remove the catalyst. The collected product was dried in a vacuum at room temperature, resulting in 356 mg of solid product.

ATRP of *n*BA (PBA). Control experiments for the polymerization of *n*-butyl acrylate initiated by HBBP were carried out in bulk to demonstrate the ATRP behavior of the system applied to the synthesis of GCNF−PBA. In a typical experiment, a dry 100 mL Schlenk flask was charged with 44.8 mg of CuBr (0.31 mmol), 64.9 μL of PMDETA (0.31 mmol), 85.2 mg of HBBP (0.31 mmol), and 2.0 g of *n*-butyl acrylate (15.6 mmol), and the mixture was degassed by three freeze−pump−thaw cycles. The flask was put into an oil bath at 70 °C. After 2 h, the viscosity of the mixture increased dramatically, and the polymerization reaction was quenched by liquid nitrogen. The mixture was dissolved in 30 mL of THF, and was passed through an alumina column to remove the catalyst. THF was removed by rotary evaporation under reduced pressure, and the polymer product was dried in a vacuum at 50 °C for 16 h. Specific reaction conditions and polymer yields for these control polymerizations are provided in Table 1.

ATRP Control Experiments with c-GCNF or c-GCNF−CO_2H. Control experiments for the polymerization of monomer in the presence of as-prepared GCNFs or oxidized GCNFs, GCNF−CO_2H, were performed for each monomer. Experimental conditions were the same as those of the ATRP of the pure monomer except that as-prepared GCNFs or oxidized GCNFs were present in a monomer/GCNF additive ratio of 10:1 w/w. The product was purified by dispersing the resulting mixture into 30 mL of THF, filtering the obtained suspension through a 0.2 μm Millipore nylon membrane, and washing the collected residue with excess THF. The dispersion−filtration−wash process was repeated six times. The filtrate was rotary evaporated to near dryness, and the polymer product was dried in a vacuum at 50 °C for 16 h. The residue was washed with MeOH three times, and was dried in a vacuum at room temperature for 16 h.

Cleavage of Poly(*n*-butyl acrylate) from GCNF−PBA. A representative cleavage reaction was performed by dispersing 0.1602 g of GCNF−PBA3 into 100 mL of toluene followed by adding 100 mL of *n*-butanol and 5 mL of concentrated sulfuric acid and refluxing the mixture at 100 °C for 9 days. The solvent was removed by rotary evaporation. The residual solid was dispersed into 100 mL of $CHCl_3$, and was extracted with water three times to remove sulfuric acid. The organic dispersion was filtered through a 0.2 μm Millipore nylon membrane, and was washed with $CHCl_3$. The filtrate was rotary evaporated to remove solvent, and was dried in a vacuum overnight at 50 °C. The molecular weight and polydispersity of the cleaved PBA were measured by GPC-MALLS; M_w =31 300, M_w/M_n=1.73 (see the Supporting Information).

Synthesis of GCNF−Poly(isobutyl methacrylate) (GCNF−PiBMA). For a typical polymerization, a 25 mL dried round-bottom flask was charged with 0.20 g of GCNF−HEBP−Br and 12.3 mg (0.124 mmol) of CuCl. The flask was sealed with a rubber septum, and was degassed and refilled with nitrogen three times. Deoxygenated acetone (4 mL) was added to the flask followed by the addition of 26 μL (0.124 mmol) of PMDETA via syringe. The mixture was sonicated for 15 min to form a uniform dispersion. After the addition of 4 mL (24.7 mmol) of deoxygenated isobutyl methacrylate via syringe, the flask was put into a 50 °C oil bath for 96 h. The reaction was quenched by liquid nitrogen, and THF was added to disperse the black solids. The product was filtered through a 0.2 μm Millipore ,ylon membrane, and was washed with THF. The dispersion−filtration−wash process was repeated six times to ensure no ungrafted polymers remained in the residue. The dark solids were then dispersed in methanol, and were filtered to remove the catalyst. The collected product was dried in a vacuum at room temperature.

ATRP of iBMA in the presence of GCNF−CO_2H (GCNF−CO_2H/PiBMA). A 25 mL dried round-bottom flask was charged with 0.20 g of GCNF−CO_2H and 12.3 mg (0.124 mmol) of CuCl. The flask was sealed with a rubber septum, and was degassed and refilled with nitrogen three times. Deoxygenated acetone (4 mL) was added to the flask followed by the addition of 26 μL (0.124 mmol) of PMDETA via syringe. The mixture was sonicated for 15 min to form a fine dispersion. Deoxygenated isobutyl methacrylate (4 mL, 24.7 mmol) was then added to the flask via syringe, and the mixture was stirred for 5 min. Finally, 30 μL (0.247 mmol) of HEBP was added via syringe, and the flask was put into a 50 °C oil bath for 20 h. The reaction was quenched by liquid nitrogen, and THF was added to disperse the black solid. The product was filtered through a 0.2 μm Millipore nylon membrane, and was washed with THF. The filtrate was passed through an alumina column to remove the catalyst, and the solvent was removed by rotary evaporation. The polymer product was dried under reduced pressure at 50 °C for 16 h. The solid residue was purified by repeated dispersion−filtration−THF washing (four times) to remove nongrafted polymers. The collected solid was dried in a vacuum at room temperature for 16 h.

ATRP of iBMA (PiBMA). A 25 mL dried round-bottom flask was charged with 12.3 mg (0.124 mmol) of CuCl. The flask was sealed with a rubber septum, and was degassed and refilled with nitrogen three times. Deoxygenated acetone (4 mL) was added to the flask followed by the addition of 26 μL (0.124 mmol) of PMDETA via syringe. Deoxygenated isobutyl methacrylate (4 mL, 24.7 mmol) was then added to the flask via syringe, and the mixture was stirred for 5 min. Finally, 30 μL (0.247 mmol) of HEBP was added via syringe, and the flask was put into a 50 °C oil bath for 20 h. The reaction was quenched by liquid nitrogen, and THF was added to dilute the mixture. Catalyst was removed by passing the solution through an alumina column, and the solvent was removed by rotary evaporation. The polymer product was dried in a vacuum at 50 °C for 16 h.

Synthesis of GCNF−Poly(*tert*-butyl acrylate) (GCNF−P*t*BA). A 25 mL dried round-bottom flask was charged with 0.20 g of GCNF−HEBP−Br and 38.7 mg (0.27 mmol) of CuBr. The flask was sealed with a rubber septum, and was degassed and refilled with nitrogen three times. Deoxygenated acetone (4 mL) was added to the flask followed by the addition of 56.6 μL (0.27 mmol) of PMDETA via syringe. The mixture was sonicated for 15 min to form an even dispersion. After the addition of 4 mL (27 mmol) of deoxygenated *tert*-butyl acrylate via syringe, the flask was put into a 60 °C oil bath for 22 h. The purification process of the product was the same as that of GCNF−PiBMA.

ATRP of *t*BA in the Presence of GCNF−CO$_2$H (GCNF−CO$_2$H/P*t*BA). A 25 mL dried round-bottom flask was charged with 0.20 g of GCNF−CO$_2$H and 38.7 mg (0.27 mmol) of CuBr. The flask was sealed with a rubber septum, and was degassed and refilled with nitrogen three times. Deoxygenated acetone (4 mL) was added to the flask followed by the addition of 56.6 μL (0.27 mmol) of PMDETA via syringe. The mixture was sonicated for 15 min to form an even dispersion. Then 4 mL (27 mmol) of deoxygenated *tert*-butyl acrylate was added to the flask via syringe, and the mixture was stirred for 5 min. Finally, 30 μL (0.27 mmol) of MBrP was added via syringe, and the flask was put into a 60 °C oil bath for 22 h. The purification process of the product was the same as that for GCNF−CO$_2$H/PiBMA.

ATRP of *t*BA (P*t*BA). A 25 mL dried round-bottom flask was charged with 38.7 mg (0.27 mmol) of CuBr. The flask was sealed with a rubber septum, and was degassed and refilled with nitrogen three times. Deoxygenated acetone (4 mL) was added to the flask followed by the addition of 56.6 μL (0.27 mmol) of PMDETA via syringe. Then 4 mL (27 mmol) of deoxygenated isobutyl acrylate was added to the flask via syringe, and the mixture was stirred for 5 min. Finally, 30 μL (0.27 mmol) of MBrP was added via syringe, and the flask was put into a 60 °C oil bath for 22 h. The reaction was quenched by liquid nitrogen, and acetone was added to dilute the mixture. Catalyst was removed by passing the solution through an alumina column, and the solvent was evaporated by rotary evaporation. The polymer product was dried in a vacuum at 50 °C for 16 h.

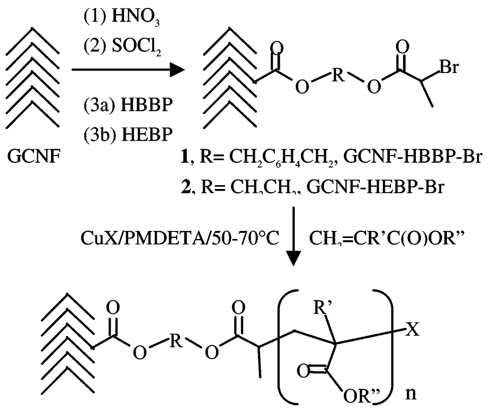
Preparation of GCNF−Poly(acrylic acid) (GCNF−PAA). Hydrophilic GCNF−poly(acrylic acid) brushes were obtained by acid hydrolysis of P*t*BA chains of the GCNF−P*t*BA sample. Typically, 50 mg of GCNF−P*t*BA was dispersed into 15 mL of CHCl$_3$ in a 25 mL flask, and 2.5 mL of CF$_3$CO$_2$H was added thereafter. The mixture was stirred at room temperature for 24 h under nitrogen protection. The reaction mixture was rotary evaporated under vacuum to remove the reagents, and the black powder of the GCNF−PAA product was collected for further characterization.

Results and Discussion

Herringbone GCNFs of ca. 150 nm average diameter were prepared in multigram quantities at 600 °C using a 7:3 Fe/Cu growth catalyst and flowing C$_2$H$_4$/H$_2$/He (4:1:1) as the carbonaceous gas following established procedures.[10a] Oxidation of GCNF surface sites by nitric acid followed by sequential reaction with thionyl chloride and either HBBP or HEBP gives GCNFs containing surface-bound ATRP radical initiators, GCNF−HBBP−Br or GCNF−HEBP−Br (see Scheme 1). The structural integrity of GCNFs is maintained throughout surface derivatization.[10b] Polymerization of acrylate monomers occurs at elevated temperature in the presence of GCNF−HBBP−Br or GCNF−HEBP−Br and CuCl or CuBr/PMDETA (*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) as catalyst. Representative reaction conditions are provided in Table 2 for several GCNF−PBA polymer brush syntheses (including polymer content).

ATRP control reactions of (1) free initiator with monomer, (2) free initiator with monomer in the presence of as-prepared GCNFs, and (3) free initiator with monomer in the presence of GCNF−CO$_2$H indicate significant radical trapping by the presence of free carbon nanofibers. In polymerizations of 2 h duration, polymer yield is reduced by ca. 40% in the presence of as-prepared GCNFs. In the presence of GCNF−CO$_2$H, a 20 h reaction time is required for achieving polymer yields comparable to those obtained from free-monomer and free-initiator syntheses.

Scheme 1. Synthesis of GCNF−Polymer Brushes



Brush	R	R'	R"	X	Abbrev.
1a	CH$_2$C$_6$H$_4$CH$_2$	H	n-Bu	Br	GCNF-PBA
2a	CH$_2$CH$_2$	Me	i-Bu	Cl	GCNF-PiBMA
2b	CH$_2$CH$_2$	H	t-Bu	Br	GCNF-PtBA
2b ↓ TFA/CHCl$_3$					
2c	CH$_2$CH$_2$	H	OH	Br	GCNF-PAA

Table 2. Typical Reaction Conditions and Polymer Content

brush **1a**	[*n*BA]:[I][a]	catalyst ratio[b]	*T* (°C)	*t* (h)	PBA wt %[c]
GCNF−PBA1	3400:1	200:1:1	70	168	11
GCNF−PBA2	3400:1	10:1:1	70	96	17
GCNF−PBA3	340:1	10:1:1	70	116	34
GCNF−PBA4	750:1	10:1:1	70	263	35

[a] Molarity of the immobilized initiator calculated by (wt GCNF−HBBP−Br × 0.115 mmol/g). [b] Catalyst ratio = [*n*BA]:[CuBr]:[PMDETA]. [c] Obtained from TGA analysis.

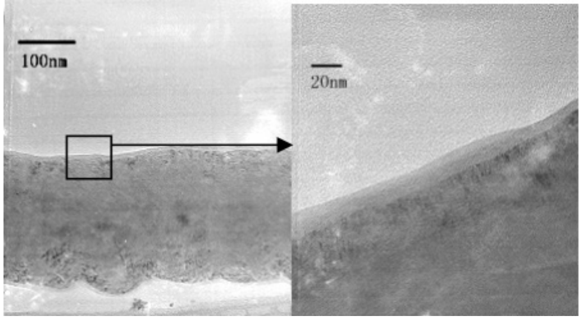


Figure 1. TEM micrographs of GCNF−PBA brush **1a** at two different magnifications.

TEM micrographs representative of GCNF−polymer brushes are shown in Figure 1 for polymer brush **1a**. A continuous polymer brush layer of 20−50 nm thickness is observed. ATRP probably occurs at various relative rates due to disparate local reaction conditions, which afford polymer brush layers of nonuniform thickness. When cleaved from the nanofiber surface and analyzed by GPC-MALLS, the polymer brush of **1a** (GCNF−PBA4) has a weight average molecular weight (M_w) of 31 300 with a polydispersity of 1.73. A polydispersity of this magnitude is consistent with diverse growth rates of individual polymer chains due to local-site heterogeneity. MWNT−PS brushes,

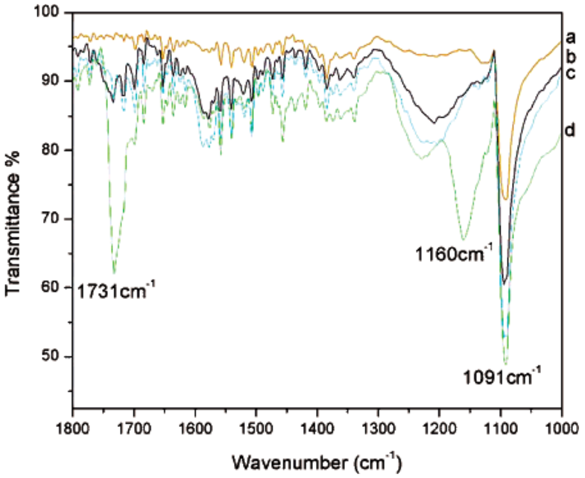


Figure 2. FT-IR spectra of (a) GCNFs, (b) GCNF−HBBP−Br, (c) GCNF−CO_2H, and (d) GCNF−PBA4.

also prepared via surface-initiated ATRP, exhibit a large polydispersity (3.08) for similar reasons.[6]

Representative changes in FT-IR spectral data for a related series of GCNF materials are shown in Figure 2. As-prepared GCNFs exhibit a strong C−C stretching band near 1091 cm^{-1} and weak bands near 1580 cm^{-1} that are assigned to graphene sheet vibrations.[16] Surface-oxidized GCNFs, GCNF−CO_2H, show carbonyl C=O stretching bands at 1716 and 1731 cm^{-1}, with increased band intensity near 1217 cm^{-1} due to the presence of C−O stretching and C−O−H bending vibrations. Covalent attachment of HBBP initiator groups to surface CO_2H sites using esterification chemistry causes few distinctive changes in the FT-IR spectrum. However, growth of the corresponding poly(acrylate) chains is evidenced by the appearance of strong bands that are characteristic of polymer functional groups. Spectra of polymer brushes **1a**, **2a**, and **2b** show strong bands at 1731 and 1160 cm^{-1} associated with C−O and C=O stretching bands of ester functional groups, whereas the carbonyl C=O stretching band shifts to ca. 1575 cm^{-1} for GCNF−poly(acrylic acid) brush **2c**.

^1H NMR spectra of PBA and of GCNF−polymer brush GCNF−PBA3 (see Figure 3) are consistent with the presence of surface-bound poly(*n*-butyl acrylate) chains in this GCNF−polymer brush material. Resonances at 0.91, 1.34, and 1.58 ppm are assigned to the *n*-butyl methyl (0.91 ppm) and methylene (1.34 and 1.58 ppm) groups within the poly(*n*-butyl acrylate) chains. Compared to the corresponding resonance intensities of PBA, the intensities of backbone proton resonances of the polymer brush are dramatically reduced because of relaxation broadening resulting from restricted motion. This phenomenon, which is related to the solidlike properties of surface-bound polymers, has been observed for related polymer brush materials, and is expected for GCNF−polymer brushes as well.[17]

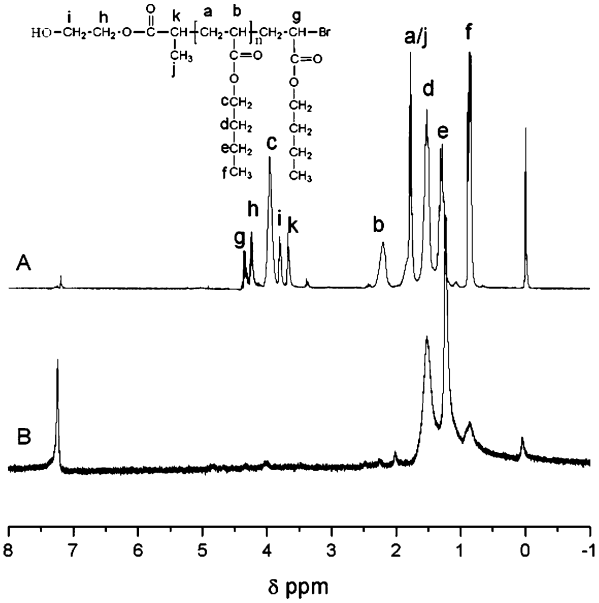


Figure 3. ^1H NMR spectra (in $CDCl_3$ solution) of (A) PBA and (B) GCNF−PBA3.

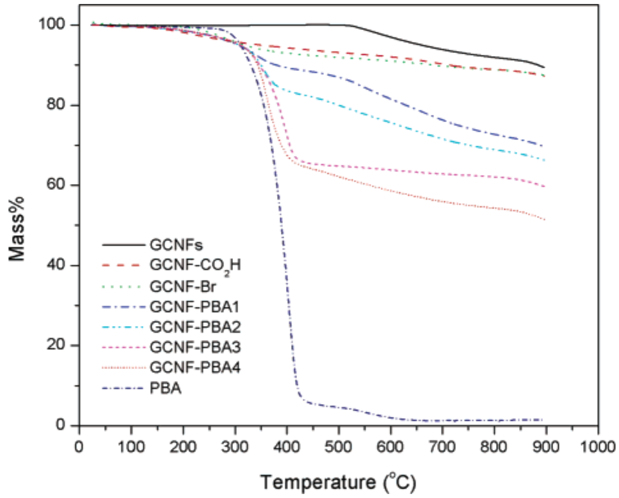


Figure 4. TGA traces of as-prepared GCNFs, oxidized GCNFs (GCNF−CO_2H), initiator-immobilized GCNFs (GCNF−Br, **1**), GCNF−PBA brushes (GCNF−PBA1 to GCNF−PBA4), and pure poly(*n*-butyl acrylate). TGA analysis was carried out under a nitrogen gas atmosphere to avoid air oxidation.

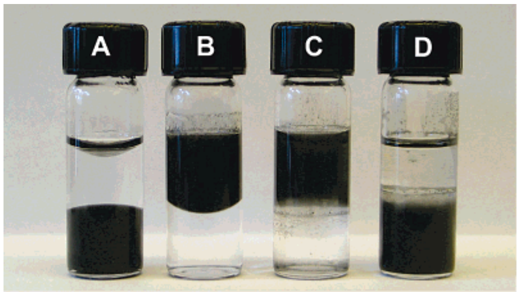


Figure 5. Dispersibilities of hydrophobic GCNF−PBA brush **1a** in water (upper)/$CHCl_3$ (lower) (vial A) and toluene (upper)/water (lower) (vial B), contrasted with the dispersibilities of hydrophilic GCNF−PAA brush **2c** in water (upper)/$CHCl_3$ (lower) (vial C) and toluene (upper)/water (lower) (vial D). GCNF−polymer brush concentrations are ca. 2 mg/mL.

TGA mass-loss curves of a family of GCNF−polymer brushes **1a** (GCNF−PBA1 to GCNF−PBA4) and related intermediate materials are shown in Figure 4. For as-prepared GCNFs, mass-loss onset occurs at 570 °C because of the excellent thermal stability of stacked graphene sheets. The 10.6 wt % mass loss from 570 to 900 °C is attributed to decomposition of randomly oxidized surface-defect sites,

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[16] Ros, T. G.; van Dillen, A. J.; Geus, J. W.; Koningsberger, D. C. *Chem.—Eur. J.* **2002**, *8*, 1151.

[17] Blum, F. D. *Annu. Rep. NMR Spectrosc.* **1994**, *28*, 277.

probably as CO/CO_2.[18] Oxidized GCNFs contain a variety of oxidized carbon species with a predominance of CO_2H functional groups. Gradual mass loss from 150−900 °C is assigned to CO and CO_2 evolution from a variety of oxygen-containing surface functional groups. Mass-loss curves for surface-bound initiator materials have profiles similar to those of oxidized GCNFs because of the small absolute mass incorporated as initiator molecules.

However, thermal decompositions of GCNF−PBA polymer brush materials occur as very evident single mass-loss events centered near 400 °C. This event parallels that observed for pure PBA, and is associated with the presence of surface-bound PBA polymer chains. The corresponding P*t*BA polymer brush **2b** thermally decomposes as two mass-loss events that also parallel those observed for pure P*t*BA (see the Supporting Information). A sharp mass loss centered at ca. 215 °C is assigned to the degradation of *t*Bu groups, whereas a broad mass loss at ca. 385 °C is consistent with the decarboxylation of ester functional groups.

Acid hydrolysis of polymer brush **2b** affords polymer brush **2c**, which contains carboxylic acid groups within each repeat unit. As shown in Figure 2, the solution dispersibility of GCNF−polymer brushes is controlled by the solubility properties of the polymer phase. Polymer brushes containing ester functional groups, such as GCNF−PBA brush **1a**, are hydrophobic, whereas polymer brush **2c**, which contains carboxylic acid groups, is hydrophilic. GCNF−P*t*BA polymer brushes form stable dispersions in $CHCl_3$ and toluene but not in water (see the Supporting Information for additional dispersibility data).

From the BET surface area of oxidized GCNFs (26 m^2/g), which best represents GCNF after oxidative etching,[10b] and from the polymer content and average molecular weight of GCNF−PBA polymer brushes, we calculate an average surface density of the polymer brush chains to be ca. 3 polymer chains/10 nm^2. As an ideal stacking pattern of graphene sheets contains ca. 120 unsaturated edge carbon atoms/10 nm^2, ca. 1 of every 40 GCNF surface edge sites is functionalized with a polymer chain. This relatively high surface functionalization accounts for the solution dispersibility properties imparted to graphitic carbon nanofibers through polymer brush formation.

Conclusions

Using surface derivatization chemistry, we can functionalize as-prepared GCNFs with ATRP initiators. Polymerization in the presence of acrylate or methacrylate ester monomers affords hydrophobic and, through ester hydrolysis, hydrophilic GCNF−polymer brush materials. By controlling both polymer brush functional group reactivity and dispersibility properties, we can now potentially make a wide range of GCNF−polymer brush hybrid composite materials accessible. In other configurations, such materials could potentially function as analyte-selective sensors for chemical- or bioagent detection. Investigation of both of these possibilities is underway.

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Supporting Information Available: Elemental analysis data, reaction conditions, TEM and AFM images, FT-IR spectra, TGA curves, dispersibility data, BET surface area analysis data, and GPC trace (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

CM051720D

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(18) Ros, T. G.; van Dillen, A. J.; Geus, J. W.; Koningsberger, D. C. *Chem.*−*Eur. J.* **2002**, *8*, 1151.