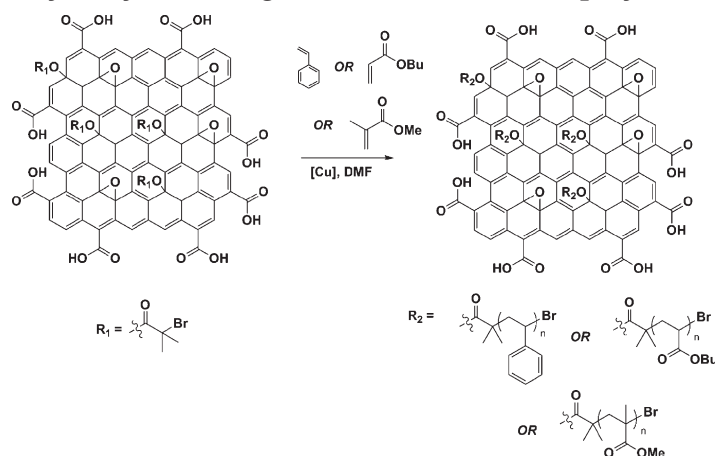


Polymer Brushes via Controlled, Surface-Initiated Atom Transfer Radical Polymerization (ATRP) from Graphene Oxide^a

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A method for growing polymers directly from the surface of graphene oxide is demonstrated. The technique involves the covalent attachment of an initiator followed by the polymerization of styrene, methyl methacrylate, or butyl acrylate using atom transfer radical polymerization (ATRP). The resulting materials were characterized using a range of techniques and were found to significantly improve the solubility properties of graphene oxide. The surface-grown polymers were saponified from the surface and also characterized. Based on these results, the ATRP reactions were determined to proceed in a controlled manner and were found to leave the structure of the graphene oxide largely intact.



Introduction

Graphene, a single-atom-thick, two-dimensional sheet of hexagonally arranged carbon atoms in the sp^2 hybridization state, displays a unique combination of electronic, chemical, and mechanical properties.^[1] These properties are expected to be fully realized when pristine, single-layer graphene sheets, typically exfoliated into thin nano- or microscale platelets from graphitic precursors, can be obtained.^[2] In order for such sheets to be utilized, however, they must be first rendered compatible with either hydrophilic or hydrophobic media; this is a current bottleneck in the graphene synthesis and modification process. Graphene oxide has been shown to function as an excellent precursor to various graphene-based materials.^[1,2] Indeed, chemical or thermal reduction of graphene oxide is considered to be one of the most practical

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approaches to economically produce graphene in large quantities. Moreover, the existence of residual oxygen-containing functional groups such as hydroxyls, epoxides, and carboxylic acids on both the basal plane and periphery of graphene oxide^[3] introduces opportunities for chemical modifications of the surface leading to improved thermal stability,^[4] mechanical robustness,^[5] and/or electrical conductivity.^[6] New methods for the exfoliation of stacked layers can also be envisioned via such an approach, and the compatibilization of graphene precursors with various types of liquid and solid media could be enhanced.

The use of non-covalent, intermolecular interactions, such as hydrogen bonding or electrostatic forces, to adhere molecular systems to extended aromatic surfaces, such as graphene oxide or graphene, is difficult to control and quantify due to the inherent instability of the resulting supramolecular systems.^[7] In contrast, the covalent attachment of functionalized, discrete small molecules^[8–10] or polymers to extended aromatic surfaces should lead to composites that are significantly more stable. Although a variety of methods have been reported for such purposes,^[11,12] they generally rely on the attachment of preformed macromolecular entities directly to the oxygenated functionalities present on the surface. Strategically, this is not ideal for steric reasons. Beyond a certain degree of functionalization, diffusion of additional molecules to the surface becomes impeded, establishing an upper limit to reactivity. Furthermore, the convoluted spatial arrangement of macromolecular species in solution may restrict access to the reactive site(s) on the surface, further reducing reactivity. In contrast, surface-initiated polymerization (SIP) from covalently immobilized initiators has been shown to be a powerful method to achieve a high degree of control over the functionality, density, and thickness of grafted materials.^[13–16] While functionalization at the graphene oxide surface may still be sterically limited, a far greater quantity of functional groups (either hydrophilic or hydrophobic) can be introduced through a SIP process, especially compared to macromolecular grafting-to approaches. Controlled radical polymerizations, particularly atom transfer radical polymerization (ATRP), are among the most-utilized methods to achieve surface-initiated polymer brushes as they provide excellent control over the polymer's molecular weight, polydispersity, and composition, and are often experimentally straightforward to perform.^[17,18]

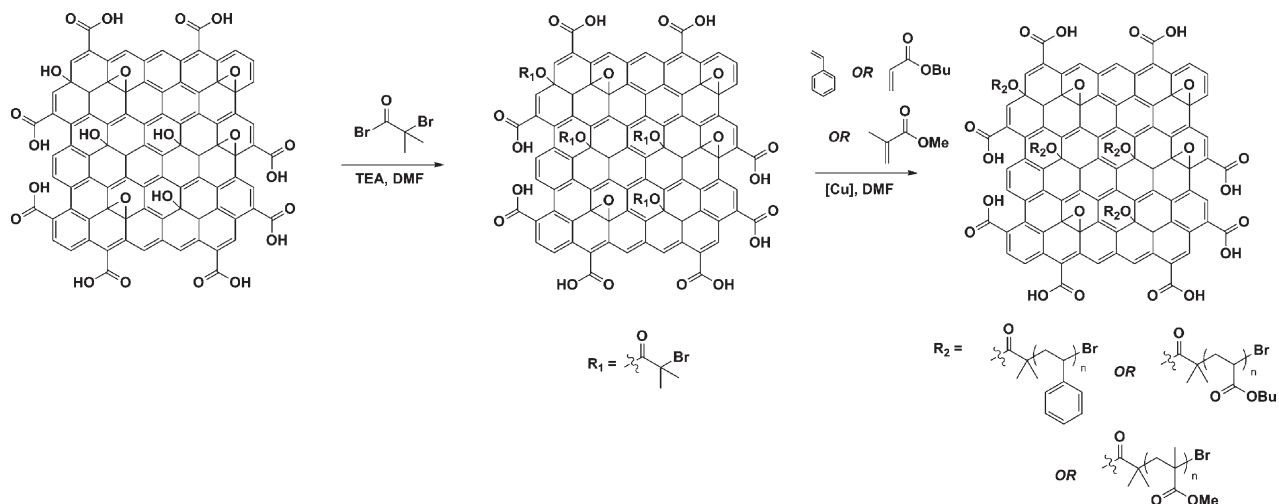
Herein, we introduce a new method for attaching polymer brushes to graphene oxide using surface-initiated ATRP. The hydroxyl groups present on the surface of graphene oxide were first functionalized with a well-known ATRP initiator (α -bromoisobutyryl bromide), and then polymers of styrene, butyl acrylate, or methyl methacrylate were grown directly via a SIP. Through subsequent characterization, the resulting polymers exhibited tunable

chain lengths and low polydispersities, indicative of controlled polymerization processes. To the best of our knowledge, SIPs from graphene oxide have not been reported^b and this is the first disclosure that offers a practical method for the controlled, covalent functionalization of graphene-based materials with synthetic polymers. Furthermore, the approach described herein is versatile and facilitates access to graphene oxide derivatives that exhibit improved dissolution properties and chemical compatibility. Such modifications have great potential for increasing the scope of processing techniques that may be used in the fabrication of modified graphenes or composites thereof.^[19–21] It is also anticipated that graphene oxide materials functionalized with ATRP initiators and, ultimately, polymers derived therefrom will be useful for controlling the surface properties of graphene-based materials, particularly for applications that require chemical and biological compatibility, wettability, or dispersibility.

Results and Discussion

The synthetic strategy employed to achieve the aim described above is summarized in Scheme 1. Graphene oxide was first treated with excess isobutyryl bromide in the presence of triethylamine (TEA) and *N,N*-dimethylformamide (DMF) in an ice bath for 24 h. Following collection via filtration, the treated graphene oxide was then vigorously washed with chloroform and deionized water to remove residual reactants. In this reaction, we envisioned the pendant hydroxyl groups on the surface of graphene oxide undergoing esterification with the acid bromide initiator. To confirm attachment, the pre- and post-functionalized graphene oxide samples were analyzed using X-ray photoelectron spectroscopy (XPS). As shown in Figure 1(a), the C-1s XP spectrum of a sample of graphene oxide (untreated with the ATRP initiator) revealed a significant degree of oxidation as numerous oxygen-containing groups were observed. However, the graphitic carbon framework retained key diagnostic signals that were attributable to the sp^2 carbons contained within the aromatic sheets. C–O bonds, and carbonyl groups (C=O), as well as carboxyl groups [C(=O)–O] were also found. After reacting graphene oxide with the aforementioned initiator, the same oxygen functional groups were still present in the

^b After submission of this manuscript, two related studies were published (see Ref.^[25,26]). The present manuscript contributes to this rapidly growing body of work by providing additional characterization of the initiator-functionalized graphene oxide, the polymer-functionalized graphene oxide, and the polymers themselves, following saponification, particularly with regard to demonstrating control of the polymerization process.



Scheme 1. Synthesis of surface-functionalized graphene oxide via attachment of an ATRP initiator (α -bromoisobutyryl bromide) followed by polymerization of styrene, butyl acrylate, or methyl methacrylate.

resulting product [Figure 1(b)], but signals attributed to the formation of C–Br bonds emerged and the intensity of the signals attributed to C–O groups diminished. Collectively, the overall change reflected a decrease in the quantity of hydroxyl groups on the surface of the graphene oxide upon esterification (as expected), a result that was subsequently confirmed via elemental analysis (Table S1 of Supporting Information). In addition, the appearance of a signal attributed to a Br-3d excitation process was observed, supporting attachment of the ATRP initiator to the surface of graphene oxide (Figure S1 of Supporting Information). From the elemental analysis results, the functionalized graphene oxide materials were calculated to contain 1.2% initiator by weight, which corresponds to approximately 33 carbon atoms per initiator, or 0.115 mmol of initiator per 100 mg of functionalized graphene oxide. Because the reaction conditions cause a slight reduction of the oxide functionality present on the surface of graphene oxide, the resulting material was expected to show improved electrical conductivity compared to unreacted graphene

oxide. Indeed, the powder conductivity of the functionalized graphene oxide was 100 times higher than that of the starting material, but still nearly three orders of magnitude lower than chemically reduced graphene oxide (CRGO; Figure S2 of Supporting Information), a benchmark material often used to compare to pristine graphene. Based on literature precedent, we believe the conductivity of the functionalized graphene oxide described above can be improved through further chemical reduction.^[2]

As illustrated in the atomic force microscopy (AFM) image shown in Figure 2(a), the functionalized graphene oxide remained as micron-sized platelets after attachment of the initiator. Although it was primarily exfoliated to monolayer platelets, a portion of the material remained as minimally layered stacks. Thermogravimetric analyses (TGA) were also performed on the surface-functionalized graphene oxide materials to assess their thermal stabilities [Figure 2(b)]. Because graphene oxide is known to store water in its π -stacked structure,^[22] and since its functionalized counterpart shares the same hydrophilic properties,

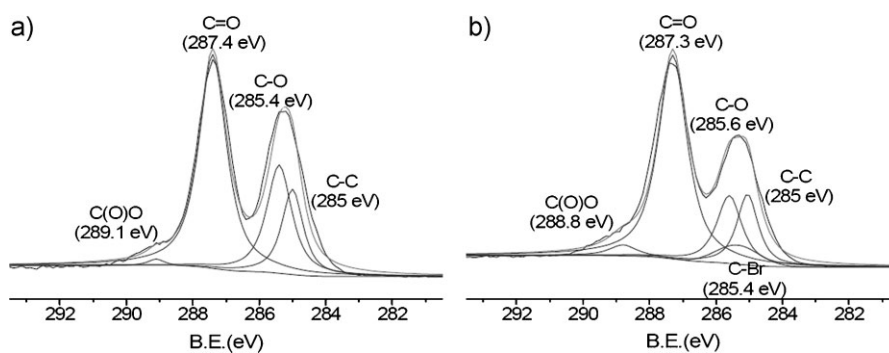


Figure 1. XPS spectra of (a) graphene oxide and (b) initiator-functionalized graphene oxide.

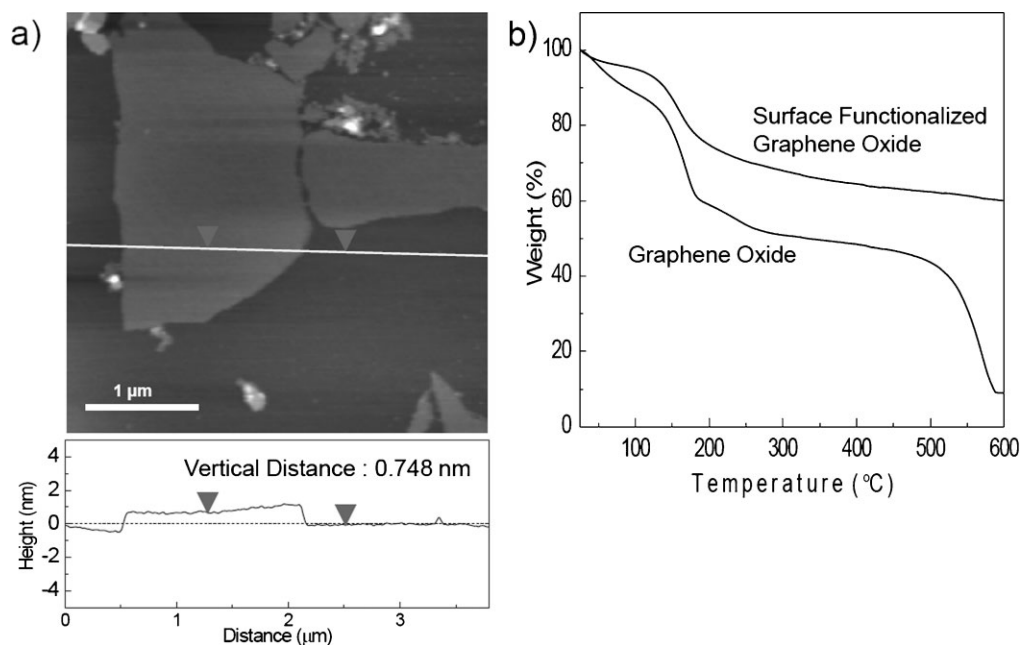


Figure 2. (a) AFM image of surface-functionalized graphene oxide showing full exfoliation, with vertical distances consistent with literature values^[27] (≈ 0.8 nm) and (b) TGA thermogravigrams of graphene oxide and surface-functionalized graphene oxide. The heating rates were $1^{\circ}\text{C}\cdot\text{min}^{-1}$ and the analyses were performed under an atmosphere of nitrogen.

some mass loss was observed near 100°C . However, a relatively large loss in mass was observed around 150°C and is believed to be oxygen-containing functional groups outgassing as carbon oxides, principally CO and CO₂. The functional groups of surface-functionalized graphene oxide, including the initiator, appear to decompose from 120 to 180°C . Notably, these decomposition processes were not observed in the thermogravigram of unfunctionalized graphene oxide. After burning out the thermally labile oxygen and initiator groups, there was no considerable mass loss up to 600°C , at which point the carbon framework appeared to undergo vaporization.

Upon synthesis and characterization of the ATRP initiator-functionalized graphene oxide, subsequent efforts focused on growing polymers from its surface in a controlled fashion. A series of polymerizations were initiated by adding monomer (either styrene, methyl methacrylate, or butyl acrylate), tris(2-aminoethyl)amine (TREN), and copper(0) (wire wrapped around a stir bar) to a DMF mixture containing the aforementioned functionalized graphene oxide material. The resulting mixtures were then stirred at 80°C for 18 h. After cooling to ambient temperature, the modified graphene oxide samples were washed with excess DMF and then dried under vacuum.

The graphene oxide materials containing surface-initiated polystyrene (SIPS) were examined in detail to investigate the properties of the polymer brushes. Figure 3(a) and (b) show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images

of the SIPS brushes on the graphene oxide surface, respectively. From these images, it appears that the functionalized platelets became wrinkled and folded during the sample preparation. However, it is also clear that the polymers covered the convoluted surfaces of the platelets and the graphene oxide was exfoliated to single-layers. These results were further supported by diffraction analysis [see inset in Figure 3(b)].

Subsequent analysis of the polymer chains via solution phase ^1H NMR spectroscopy verified that the polymerizations from the functionalized graphene oxide surfaces were successfully conducted for all the monomers investigated [Figure 3(c)]. Using end-group analysis, an absolute number average molecular weight (\bar{M}_n) of 17 kDa was calculated for polystyrene (SIPS 1; see below). This result was representative of the results collected for other samples and indicates that polymerizations were successfully initiated from the surface of graphene-based materials.

Despite being covalently attached to synthetic polymers, the Raman spectra of graphene oxide, initiator-functionalized graphene oxide and SIPS all showed the characteristic^[23] tangential mode signals (G band) and disorder mode signals (D band) at $\nu = 1600$ and 1358 cm^{-1} , respectively (Figure S3 of Supporting Information). In addition, the D/G ratio for graphene oxide, surface-functionalized graphene oxide, and SIPS was nearly constant at 1.2.^[24] The solubility of the polymer-functionalized graphene oxide proved to be dependent on the type and chain length of polymer, as well as the concentration of the composite. The SIPS material

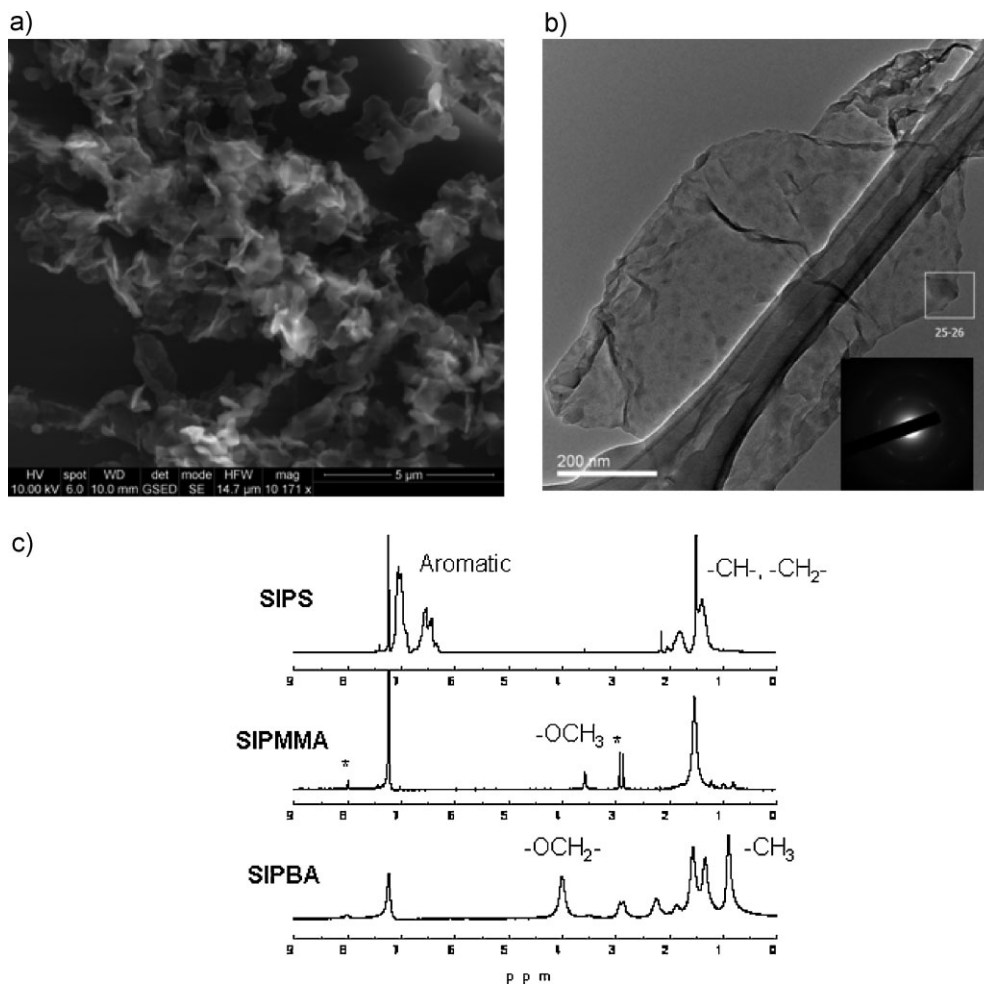


Figure 3. (a) SEM showing wrinkling of the polymer-functionalized graphene oxide and (b) TEM images of the polymer brushes grown from initiator-functionalized graphene oxide surfaces (inset: diffraction pattern of box area indicates single-layer graphene oxide). (c) ^1H NMR spectra (500 MHz, CDCl_3) of PS (labeled SIPS), PMMA (labeled SIPMMA), and PBA (labeled SIPBA) (top to bottom) grown from surfaces of graphene oxide (* indicates residual solvent peaks (DMF)).

was found to be soluble in both polar and relatively non-polar organic solvents including DMF, toluene, chloroform, and methylene chloride, up to $30 \text{ mg} \cdot \text{mL}^{-1}$ and stable for more than one week in chloroform. The longest preservation time was more than three months at $10 \text{ mg} \cdot \text{mL}^{-1}$ of SIPS in chloroform. Furthermore, the UV-vis absorbance of SIPS increased proportionally with respect to the concentration of the polystyrene, obeying Beer's Law, as shown in Figure S4 of Supporting Information. Notably, the glass transition temperature (T_g) of the tethered polymer was found to be 103°C , a modest 5°C increase with respect to a commercial sample of polystyrene homopolymer. Hence, the attachment of graphene oxide appears to have minimal effect on the thermal properties of the attached polymer.

To examine the ability to control the chain lengths of the polymer grown from the surfaces, we varied the quantity of the loaded monomer (1.0 to 5.0 mL of styrene) relative to a

fixed amount of initiator-functionalized graphene oxide (100 mg). In particular, SIPS 1–5 were prepared with 1.0, 2.0, 3.0, 4.0, and 5.0 mL of styrene, respectively, and 100 mg of initiator-functionalized graphene oxide. At the same concentration of SIPS in DMF (in $\text{mg} \cdot \text{mL}^{-1}$), the sample with the shortest polymer chains contained the largest amount of graphene oxide (relative to polymer). As a result, this material appeared as the darkest colored solution. As shown in Figure 4(a), the absorption of the SIPS materials became less intense with higher loadings of styrene. The relative composition of the two components was confirmed by TGA [Figure 4(b)], which showed higher residual mass for lower loadings of monomer. The residual mass at 500°C was determined to be 35.2% for SIPS 1 which sequentially stepped down to 8.5% for SIPS 4 in accordance with the molecular weight of the attached PS. In our hands, the residual mass of pure PS, as determined by TGA, was found to be 4.2%.

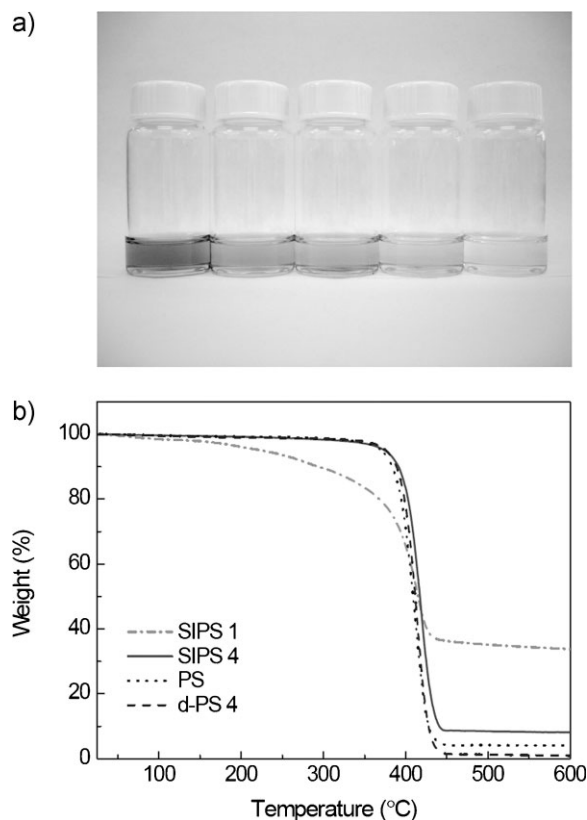


Figure 4. (a) Visualization of the solubility of SIPS with different chain lengths in DMF. The concentration of SIPS is $0.3 \text{ mg} \cdot \text{mL}^{-1}$ for all samples, from left-to-right: SIPS 1, SIPS 2, SIPS 3, SIPS 4 and SIPS 5. (b) Thermogravigrams of SIPS, PS, and detached PS from SIPS (d-PS) under nitrogen. The residual mass at $500 \text{ }^\circ\text{C}$ was 35.2% for SIPS 1, 8.5% for SIPS 4, 4.2% for PS, and 1.3% for d-PS 4.

To characterize the grafted polymers, the surface-attached polystyrene chains were detached from the graphene oxide surface via saponification with sodium hydroxide in DMF. As shown in Figure 5, the molecular weights of detached polystyrene (d-PS) increased in accordance with the amount of monomer loaded (i.e. d-PS 1–5 were detached from SIPS 1–5, respectively), as determined using gel permeation chromatography (GPC). In addition, the detached polymers were found to exhibit relatively low polydispersities (PDIs typically less than 1.5) which suggested to us that the aforementioned SIPS proceeded in a controlled manner, despite the fact that the polymerizations were initiated and conducted from a surface. The theoretical molecular weights were calculated based on the initial initiator concentration with respect to virgin graphene oxide material using elemental analysis and were in good agreement with their experimentally determined values. The detachment of polystyrene was further confirmed using TGA. For example, the residual mass of d-PS 4 was 1.3 wt.-%, reflecting the complete separation of the polymer from its graphene oxide support. Finally, the \bar{M}_n s of SIPS were consistently larger than that of

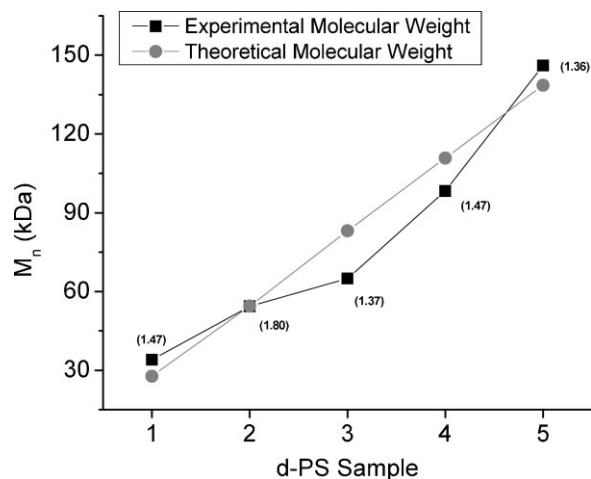


Figure 5. GPC-measured \bar{M}_n of d-PS prepared from different monomer to initiator-functionalized graphene oxide ratios. d-PS 1–5 were prepared from 100 mg of initiator-functionalized graphene oxide and either 1.0, 2.0, 3.0, 4.0, or 5.0 mL of styrene, respectively. Values in parentheses reflect the PDIs of the d-PS samples. Theoretical molecular weights were calculated from the monomer-initiator ratio (the initiator content determined from elemental analysis results; see Table S1 of Supporting Information).

d-PS due to the presence of covalently attached graphene oxide. For example, the \bar{M}_n of SIPS 5 was measured at 157 kDa; a value that was measurably higher than that observed for d-PS 5 (146 kDa). Based on the differential molecular weight, the content of graphene oxide in SIPS 5 was calculated to be 7 wt.-%.

Experimental Part

Preparation of Initiator-Functionalized Graphene Oxide

Graphene oxide was prepared from purified flake graphite (SP-1, Bay Carbon, Inc.) using a modified Hummers method.^[2] Graphene oxide (1.00 g) and DMF (30 mL, Sigma–Aldrich) were loaded in a round bottom flask and sonicated for 1 h to prepare a colloidal suspension of graphene oxide. TEA (20 mL, Fisher Scientific) and α -bromoisobutyryl bromide (30 mL, Fluka) were then added to the flask immersed in an ice bath and the resulting solution was stirred for 24 h. The product was collected via filtration over a medium fritted glass funnel, washed with chloroform ($6 \times 150 \text{ mL}$, Aldrich) and deionized water ($1 \times 150 \text{ mL}$), and then dried under high vacuum for 18 h.

Atom Transfer Radical Polymerization (ATRP) of Polymer Brushes from the Surfaces of Graphene Oxide

Initiator-functionalized graphene oxide (100 mg), monomer [styrene (1.0, 2.0, 3.0, 4.0, or 5.0 mL), methyl methacrylate (5 mL) or butyl acrylate (2.5 mL)], tris(2-aminoethyl)amine (75 μL), DMF (5 mL), and a small piece of copper(0) wire wrapped around a stir bar were

loaded into a sealed vial and stirred at 80 °C for 18 h. The resulting viscous solution was then poured into ethanol (50 mL) to precipitate the product and to remove residual monomer and reactants. After washing the filtrate with ethanol (2 × 150 mL), the light gray product was dried under vacuum, dissolved in DMF (50 mg · mL⁻¹), and then centrifuged for 30 min. The supernatant was filtered through a 0.02 μm Anodisc membrane filter (Whatman), washed with DMF, precipitated again in ethanol, and then dried under vacuum for 18 h.

Saponification of Polymer Chain from the Surfaces of Functionalized Graphene Oxide

Sodium hydroxide (300 mg) was combined with a solution of SIPS in DMF (5 mg · mL⁻¹; 5 mL of DMF) and the resulting mixture was stirred at 80 °C for 7 d. The opaque solution was then filtered through a 2.0 μm polycarbonate membrane filter (Whatman). The filtrate was poured into excess ethanol, which caused a solid to precipitate. The isolated solids were then washed with ethanol (2 × 50 mL) and deionized water (2 × 50 mL) to remove residual base. The resulting material was then vacuum-dried, dissolved in DMF (final concentration = 10 mg · mL⁻¹), and filtered through a 0.2 μm PTFE syringe filter before being analyzed via GPC.

Characterization

Elemental analyses were performed by Atlantic Microlab, Norcross, GA, USA. ¹H NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer. All ¹H NMR spectra were referenced to residual protio solvent measured downfield from TMS (CDCl₃: 7.24 ppm). Thermogravimetric analysis (TGA) data were obtained by ramping from 25 to 800 °C under a nitrogen atmosphere using a Mettler Toledo TGA/SDTA 851. The temperature ramp rates were 1 °C · min⁻¹ for graphene oxide and initiator-functionalized graphene oxide and 10 °C min⁻¹ for SIPS and d-PS. Glass transition temperatures were measured using a Mettler Toledo DSC 823e by ramping from 25 to 250 °C at 10 °C · min⁻¹. XPS measurements were performed using a Kratos AXIS Ultra DLD spectrometer. Molecular weights were determined using a Waters 1515 isocratic HPLC pump fitted with two fluorinated polystyrene columns (I-MBHW-3078 and I-MBLMW-3078, Viscotek) thermostatted to 40 °C (using a ELDEX CH 150 column heater) and arranged in series with a Waters 2414 refractive index detector. The reported \bar{M}_n s were based on polystyrene standards. TEM images were taken on a JEOL2010F micrograph at 120 and 200 keV in a bright field mode. UV-vis spectra were recorded on PerkinElmer Lambda35 spectrometer. SEM images were taken using a Quanta F600 ESEM equipped with a 500 micron gaseous secondary electron detector (GSED) in an environmental SEM (ESEM) mode at water pressures ranging from 0.83 to 0.98 Torr using a spot size 6 at 10 keV. AFM images were recorded on a Park Scientific AutoProbe CP/MT (MultiTask) instrument with scans obtained in contact mode. Micro Raman measurements of modified graphene oxide and SIPS samples were performed using a WiTec Alpha300 system with a 532 nm wavelength incident laser light.

Conclusion

In summary, we have demonstrated a facile method to functionalize the surface of graphene oxide using ATRP. The morphology of the resulting polymer brushes was studied using AFM and TEM, while the polymers themselves were characterized by NMR, GPC, DSC, and TGA. Elemental analysis, Raman spectroscopy, and XPS were used to confirm attachment of the initiator to the graphene oxide surface in addition to various solubility studies. These results indicate that both the polymers and the graphene oxide retained structural features seen in virgin samples. Importantly, this functionalization strategy was shown to significantly increase the solubility of the resulting materials, allowing for chemical characterization and modifications to be performed in a single, homogeneous phase. Increased solubility/dispersability may also enhance the processing potential of these materials for applications in polymer composites. Polymerization with more sophisticated monomers using the method reported herein may provide an expeditious route to tuning the physical, thermal, and electrical properties of graphene and its related compounds.

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