



# Graphene oxide modification with graft polymers via nitroxide mediated radical polymerization



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## ABSTRACT

We demonstrate a method to modify the surface of graphene oxide (GO) by grafting polymer chains using nitroxide mediated radical polymerization (NMRP). Surface modification by NMRP was achieved using GO functionalized with 2,2,6,6-tetramethyl-piperidine 1-oxyl (TEMPO, T) to produce graphene oxide-TEMPO (GO-T). GO prepared from graphite by the Hummer's method was facilely functionalized in one step with T. Graft polymerization reactions of styrene and isoprene were carried out using nitroxide chemistry to control the polymerization and the 'grafting from the surface' polymerization technique. GO-T acts as a multifunctional macroalkoxyamine initiating and controlling the polymerization in the presence of monomer. The grafting reactions were performed by dispersing GO-T in dimethylformamide and heating at 130 °C in the presence of monomer to form graphene oxide-g-polystyrene-TEMPO (GO-g-PS-T) and graphene oxide-g-polyisoprene-TEMPO (GO-g-PI-T). FT-IR, Raman, XPS, XRD, TGA and TEM data are consistent with the attachment of the TEMPO group to the GO surface and with polystyrene and polyisoprene being grafted onto the GO surface. The amount of PS and PI grafted to GO-T was estimated from TGA data to be approximately 34% for a 7 h reaction time and 68% for a 144 h reaction time, respectively.

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## 1. Introduction

Research in the physics, chemistry and biological applications of graphene type materials is currently of broad and intense interest and growing exponentially. The chemical and physical modification, nanoscale manipulation and hierarchical structure building of graphenes are areas that will continue to impact research and applications across a broad spectrum of inter- and multi- disciplinary fields. Several excellent reviews for chemically modifying graphene and its oxides along with applications of the materials can be found in recent works by Liu et al. [1], Salavagione et al. [2], Kuila et al. [3,4], and others [5–11]. Graphenes offer a vast potential for modification due to their two-dimensional, one-atom thick, sheet-like structure of  $sp^2$  hybridized carbon atoms. In oxidized forms, graphenes bear a number of chemically addressable groups such as OH, COOH and epoxy C–O–C. New techniques and strategies for

the chemical modification of graphene or graphene oxide (GO) are of paramount importance to advance the understanding of these bertholoid type materials and to contribute to the growth and development of hierarchical graphene structures for applications in areas such as electronics, photonics and nanobiomedicine.

One strategy that is gaining recognition for modifying graphenes is grafting polymerization. This approach has been a viable route for producing carbon nanocomposites in general. For graphenes in particular, Feng, et al. [12] decorated the surface of GO with N-vinylpyrrolidone using GO itself as the polymer initiator and obtained a readily dispersible GO species.

Only a few studies have appeared on graphene modification with graft polymer chains involving a controlled radical polymerization (CRP) technique. Deng et al. [13] reported on an efficient way to functionalize graphene sheets with pre-synthesized polymer using a combination of atom transfer nitroxide radical coupling (ATNRC) chemistry with the grafting-onto strategy. GO treated with  $SOCl_2$  was used as an intermediate to which 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was anchored as part of the ATNRC chemistry. In another approach, Lee, et al. [14] reported on a method for growing polymers directly from the surface of GO

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by covalently attaching an initiator and then carrying out the polymerization of styrene, methyl methacrylate, and butyl acrylate using atom transfer.

GO surface modification has also been accomplished via radical addition-fragmentation chain-transfer polymerization (RAFT) using certain dithio compounds. The dithio modified GO materials act as highly efficient reversible addition-fragmentation chain-transfer agents, which, in the presence of initiator and monomer, provide the graft polymerization on the surface of GO. Li et al. [15] reported the GO modification with molecularly imprinted polymer; Zhang et al. [16] carried out the modification of GO with poly(*N*-vinylcarbazole); Etmimi et al. [17] synthesized polystyrene-graphite nanocomposites via miniemulsion polymerization; Jiang et al. [18] grafted polystyrene, poly(*N*-isopropylacrylamide), poly(*N,N*-dimethylacrylamide), poly(*N*-acrylomorpholine), poly(*m*-methylacrylate), and poly(*t*-butyl acrylate) to GO. By comparison with NMRP, RAFT could allow the modification of GO with a wider range of monomers (except for methacrylic monomers) at lower temperature. Its use, however, could be compromised by the need of further purification of the final polymer to eliminate color and odor as well as intellectual property issues.

In 2011 we presented preliminary results on the first reported modification of graphene oxide with graft polymers via nitroxide mediated radical polymerization using a two-step procedure involving (1) the application of an oxoammonium salt (Br-TEMPO) to surface modify GO with TEMPO and (2) the styrene graft polymerization reaction from the GO-T surface [19]. Recently, Avila-Vega and coworkers [20] used a similar technique to step 1 for the functionalization of GO with TEMPO following our procedure. The resulting materials, which consisted of exfoliated TEMPO functionalized GO, were incorporated into poly( $\epsilon$ -caprolactam) (Nylon 6) through electrospinning and resulted in new nanocomposites with improved tensile strength. Additionally, these authors suggest several mechanisms to explain the covalent bonding of the TEMPO moieties to the GO surface based on XRD analysis, although the proposed mechanisms are still speculative in nature as the demonstration of these chemical routes would require additional direct evidence not easily obtained.

We report here the results of our research on the surface modification of GO by graft polymerization reactions of styrene and isoprene using the 'grafting from' polymerization technique via nitroxide mediated radical polymerization (NMRP) chemistry, which has the potential to initiate and control the polymerization. The resulting polystyrene and polyisoprene nanocomposites were characterized by Fourier transform infrared (FT-IR), Raman and X-ray photoelectron (XPS) spectroscopies, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). Data so obtained are consistent with the attachment of the TEMPO group to the GO surface and with polystyrene and polyisoprene being grafted onto the GO surface to produce easily exfoliated graphene oxide polymer nanocomposites.

## 2. Experimental

### 2.1. Materials

Acetone (95%) and methanol (95%) were obtained from C.J. Baker and used as received. Carbon tetrachloride ( $\text{CCl}_4 \geq 99.5\%$ ), *N,N*-dimethylformamide (DMF, 99.8%), graphite, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 99%), bromine ( $\text{Br}_2$ , 99.9%) and triethylamine (TEA, 99.5%), were obtained from Aldrich and used as received. The inhibitor in styrene (Aldrich, 99%) was removed by vacuum distillation over  $\text{CaH}_2$ , and that in isoprene (Aldrich, 99%) by atmospheric distillation (84.6 kPa, Saitillo, Mexico).

### 2.2. Measurements

FT-IR spectra of the samples as KBr pellets were measured with a Nexus 470 Spectrometer over  $4000\text{--}400\text{ cm}^{-1}$  using 50 scans and  $4\text{ cm}^{-1}$  of resolution in transmission mode. TGAs were performed using a Q500 TGA analyzer by heating the samples of  $<10\text{ mg}$  at  $10\text{ }^\circ\text{C}/\text{min}$  from 30 to  $600\text{ }^\circ\text{C}$  under a nitrogen flow rate of  $50\text{ mL}/\text{h}$  and under an oxygen flow at the same rate from  $600$  to  $800\text{ }^\circ\text{C}$ . XRD analyses were performed on a Siemens D-5000 operated at 35 kV and 25 mA and using Cu  $K\alpha$  radiation and an aluminum standard. XPS experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source (Mg  $K\alpha$  line of  $1253.6\text{ eV}$  and an applied power of 250 W and calibrated using the  $3d_{5/2}$  line of Ag with a full width at half maximum (FWHM) of  $1.1\text{ eV}$ ). An electron flood gun was used to compensate for charging during XPS data acquisition. The selected resolution for the spectra was 30 eV of Pass Energy and 0.5 eV/step for the general survey spectra and 15 eV of Pass Energy and 0.15 eV/step for the detailed spectra of the different elements. All measurements were made in an ultra-high vacuum (UHV) chamber at a pressure of about  $5 \times 10^{-8}\text{ mbar}$ . Gaussian-Lorentzian functions were used to perform the curve fitting of the high resolution spectra. Raman data were recorded at room temperature using a Renishaw RM1000 Laser Raman Microscope at a wavelength of 532 nm, 50% laser. Electron microscopy analyses were performed with an FEI Titan 80–300 kV (TEM) and a JEOL JSM-7401F (SEM) instruments. Elemental analyses were performed by Galbraith Labs, Inc., Knoxville, TN, USA.

### 2.3. Preparation of GO-T, GO-g-PS-T, and GO-g-PI-T

The synthesis schemes for graphene oxide-TEMPO (GO-T), graphene oxide-g-polystyrene-TEMPO (GO-g-PS-T), and for graphene oxide-g-polyisoprene-TEMPO (GO-g-PI-T) are shown in the Scheme. Graphene oxide was prepared by the Hummers method [21]; Br-TEMPO was synthesized according to Bonilla-Cruz et al. [22,23].

For the preparation of GO-T, GO (0.4 gr) was dispersed in 400 mL of DMF; a solution of Br-TEMPO (0.0156 mol in 40 mL of DMF) was then added drop wise to the dispersion in the presence of triethylamine (0.0234 mol) used to trap the HBr formed during the reaction. The reaction system was then saturated with argon and stirred for 48 h at room temperature. GO-T was purified by four alternating cycles of centrifugation at  $18,866 \times g$  (20 min) and washes with DMF to remove residual Br-TEMPO and eliminate the possibility of a GO TEMPO mixture. The GO-T was then lyophilized for 24 h. The GO and GO-T were analyzed by XRD, FT-IR, TGA, Raman, XPS, elemental analysis and TEM.

The graft polymerization of styrene was carried out in a jacketed glass reactor. 24 mg of GO-T were dispersed in 24 mL of DMF with ultrasonication for 30 min. Subsequently, the dispersion and styrene (1 mL, 0.9 g, 0.0086 mol) were fed to the reactor. The system was deoxygenated with nitrogen for 30 min. The temperature was then increased to  $130\text{ }^\circ\text{C}$  and the mixture stirred. After 7 h, the polymerization were stopped. The dispersions were subjected to four alternating cycles of centrifugation at  $18,866 \times g$  (20 min) and washes with DMF to separate the free polystyrene from GO-g-PS-T. Finally GO-g-PS-T was washed with methanol. The GO-g-PS-T was dried under vacuum and analyzed by XRD, FT-IR TGA, TEM, XPS, and Raman spectroscopy.

For the isoprene graft polymerization, 18 mg of GO-T were dispersed in 18 mL of DMF with ultrasonication for 30 min. The dispersion and the monomer (1.10 mL, 0.75 g, 0.011 mol) were fed to a stainless steel reactor. The system was deoxygenated with nitrogen for 30 min and pressurized at 150 psi absolute. When the

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