



Covalent modification of graphene oxide with polynorbornene by surface-initiated ring-opening metathesis polymerization



Qiuping Zhang, Qing-Lan Li, Shidong Xiang, Yan Wang, Chunyang Wang, Wei Jiang, Hang Zhou, Ying-Wei Yang*, Jun Tang*

College of Chemistry, State Key Laboratory for Supramolecular Structure and Materials, Jilin University, Changchun, Jilin 130012, PR China

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ABSTRACT

Surface-initiated ring-opening metathesis polymerization (SI-ROMP) was employed to prepare polymer-grafted graphene oxide (GO). Grubbs catalysts were immobilized onto GO surfaces followed by ROMP of norbornene from these active catalyst sites to result in polynorbornene (PNb)-functionalized GO (GO-PNb), whose structure and morphology were fully characterized by FTIR, Raman, NMR, XRD, TGA and SEM. The as-prepared hybrid material of GO-PNb is an intercalated layer structure with an improved solubility in organic solvents. Further epoxidation of double bonds along the PNb chains resulted in the epoxidized PNb-functionalized GO (GO-ePNb). The relatively low and irregular grafting ratio of PNb on GO measured by gravimetry mainly result from the effect of complex GO surfaces and the chain-transfer reactions in the polymerization process.

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1. Introduction

Owing to its unique two-dimensional layered structure and remarkable properties [1], graphene oxide (GO) has already gained considerable attention and shown potential applications in the fields of energy storage [2–4], electrochemical devices [5,6], catalysis [7], cell imaging [8], drug delivery [9,10], biomedicine [11] and others [12–16]. However, its poor dispersion and low stability in non-polar organic solvents bring many difficulties for its widespread real applications. In order to obtain advanced functional GO materials with alluring properties, efficient GO surface modification methods are still in urgent need. A number of reports have demonstrated the feasibility of the modification of GO through different type of covalent and non-covalent functionalization approaches [17–21]. Among them, covalent functionalization of GO with polymers, *via* a “grafting to” [22–24] or “grafting from” method [25,26], has proved to be the most promising approaches. For the “grafting from” method, surface initiated polymerization (SIP) presents a versatile and an effective approach for substrate modification due to the control over the density, functionality, thickness and composition of the grafted polymers although this approach needs an extra step to introduce the initiating groups

onto GO sheets before polymerization. During the past few years, GO has been modified with various polymers by SIP in a controllable polymerization manner, such as atom transfer radical polymerization (ATRP) [27–32], ring opening polymerization (ROP) [33], reversible addition fragmentation chain transfer (RAFT) polymerization [34], redox polymerization [35] and other polymerization approaches [36]. As a consequence, the structures and properties of GO could be effectively improved and GO can be endowed with novel properties after grafting with polymers.

Recently, ring-opening metathesis polymerization (ROMP) has become a powerful and broadly applicable method for surface modification of substrates owing to its mild reaction conditions, functional group tolerance and further functionalization with the double bonds along the resulting polymer chains. In 1999, Grubbs et al. [37] first reported the surface-initiated ROMP (SI-ROMP) of norbornene derivative from gold surface with Grubbs 1st generation catalyst. Subsequently, many reports displayed the successful SI-ROMP from various surface including silicon wafers [38], silica nanoparticles [39], carbon nanotubes [40], carbon paper [41], cellulose fibers [42], montmorillonite clay [43] and other substrates [44], suggesting that ROMP is an important polymerization strategy for the synthesis of a variety of polycycloolefins, such as polynorbornene (PNb), as non-polar polyolefins that can be introduced onto polar materials to effectively tailor the performance of substrates. Our research group recently reported the successful preparation of the surface-bound PNb films from Si/SiO₂ substrates by SI-ROMP, and described a strategy to prevent the degradation

* Corresponding authors. Fax: +86 431 88498179.

E-mail addresses: ywyang@jlu.edu.cn (Y.-W. Yang), chemjtang@jlu.edu.cn (J. Tang).

during the epoxidation of grafted PNB chains just by solvent effect under mild conditions [45].

In this paper, we demonstrate a functionalization approach to grow polymers from GO sheets by SI-ROMP for the first time. Considering the oxygen-containing functional groups on GO sheets [46], we use highly efficient Grubbs catalyst for ROMP because of its excellent functional group tolerance and remarkable selectivity of olefins [47,48]. For the current study, norbornene has been chosen as a model monomer for polymerization because of its commercial availability and high ring strain for driving the polymerization process [49]. Herein, norbornenyl initiator ligands were covalently attached onto GO surfaces by esterification, and the Grubbs catalyst was then employed onto GO, followed by ROMP from the effective catalyst sites on GO with norbornene monomers at room temperature, resulting in GO-PNB. Finally, GO-PNB was further modified by epoxidation of carbon double bonds along PNB chains. It is worth noting that the polymers synthesized by ROMP could be further functionalized to generate more novel polymers [50–54]. Therefore, the modification of GO with ROMP is a promising versatile strategy, which may broaden the application scope of ROMP and provides a new choice for the covalent modification of GO with polymers.

2. Experimental section

2.1. Materials

Natural graphite powder was purchased from Tianjin Guangfu Fine Chemical Research Institute. 5-Norbornene-2-carboxylic acid (NBE), benzylidenebis(tricyclohexylphosphine)dichloro-ruthenium (Grubbs 1st generation catalyst), (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinyldiene)dichloro(phenylmethylene)(-tricyclohexylphosphin-e)ruthenium (Grubbs 2nd generation catalyst), norbornene, ethyl vinyl ether, meta-chloroperoxybenzoic acid (MCPBA) were purchased from Sigma–Aldrich and used without further purification. 5-Norbornene-2-acyl chloride was synthesized according to a literature procedure [55]. Tetrahydrofuran (THF) was purchased from Beijing Chemical Works and dried from the blue Na/benzophenone ketyl solution prior to use. All other reagents and solvents were purchased from commercial suppliers and used as received unless otherwise noted.

2.2. Preparation of GO

GO was synthesized from natural graphite powder by a modified Hummers method [56,57]. The dispersion of crude GO in water was subjected to dialysis to completely remove acids and metal ions. Then GO was obtained by lyophilization.

2.3. Preparation of norbornene-functionalized GO (GO-NBE)

GO (85 mg) and freshly distilled THF (17 mL) were added in a 50 mL round bottom flask, followed by treating with an ultrasonic bath for 1 h. Subsequently, triethylamine (Et_3N) (870 μL , 6 mmol) and 5-norbornene-2-acyl chloride were added into the mixture in an ice-water bath, and then the mixture was slowly heated to room temperature for 48 h. The mixture was separated by repeated centrifugation, resuspension with distilled water and THF, and then dried in vacuum to give the final product of GO-NBE.

2.4. Preparation of polynorbornene-functionalized GO (GO-PNB)

Firstly, catalyst-functionalized GO (GO-[Ru]) was synthesized. The GO-NBE (25 mg) and freshly distilled THF (5 mL) were added into a 25 mL round bottom flask. The mixture was sonicated for

30 min, and bubbled with nitrogen for 5 min, then a solution of Grubbs 1st generation catalyst (15 mg, 1.8×10^{-2} mmol) in freshly distilled THF (1 mL) was added. The suspension was stirred at room temperature for 25 min. Subsequently, the mixture was separated by repeated centrifugation and resuspension with freshly distilled THF, resulting in the final product of GO-[Ru]. Secondly, GO-PNB was prepared by the polymerization of norbornene. The as-prepared GO-[Ru] was dispersed in freshly distilled THF (5 mL) by sonication for 10 min and bubbled with nitrogen for 3 min, followed by the addition of a THF solution of norbornene. The suspension was stirred at room temperature for 30 min, and then isolated by repeated centrifugation and resuspension with THF to remove the unreacted monomer and free polymers until there was no precipitate formed when drops of supernatant were added into methanol. The product was dried under vacuum at 30 °C for 12 h.

2.5. Preparation of epoxidized polynorbornene-functionalized GO (GO-ePNB)

The GO-PNB (20 mg) and dichloromethane (CH_2Cl_2) (10 mL) were added into a 25 mL round bottom flask. The mixture was sonicated for 30 min, then a solution of meta-chloroperoxybenzoic acid (MCPBA) (0.5 g) in CH_2Cl_2 (5 mL) was added. The suspension was stirred at room temperature for 2 h. After epoxidation, the mixture was isolated by repeated centrifugation and resuspension with CH_2Cl_2 and H_2O and then dried under vacuum at 30 °C for 12 h.

2.6. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a SHIMADZU FTIR-8400 spectrometer at a resolution of 4 cm^{-1} in a wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$ and averaged over 32 scans at room temperature. The samples were prepared using powder-pressed KBr pellets. Raman spectra were recorded on a Renishaw InVia Reflex spectrometer at 514 nm nano-argon ion laser. All powder samples were deposited on the quartz glass directly in the absence of solvents. Nuclear magnetic resonance (NMR) spectra were performed on a Bruker Avance III NMR spectrometer with CDCl_3 as solvent, operating at 400 MHz for the corresponding ^1H nuclei chemical shifts (in ppm) were reported downfield using trimethylsilane as internal standard. The powder X-ray diffraction (XRD) measurement was performed on a Rigaku D/max-II B X-ray diffractometer with monochromatic $\text{Cu } K_\alpha$ source at room temperature. The data were collected from 5° to 60° at a scan rate of $15^\circ \text{ min}^{-1}$. The interlayer distance was calculated from the 2θ values using the Bragg's law. Scanning electron microscopy (SEM) images were captured on a Hitachi FE-SEM S-4800 instrument (Japan) at an acceleration voltage of 3 kV. The samples were prepared by depositing sample dispersion onto a freshly cleaved silicon wafers surface. The grafting ratio of polymer was calculated, based on an equation of $[m(\text{GO-PNB}) - m(\text{GO-NBE})]/m(\text{GO-NBE}) \times 100\%$, by gravimetry, which was taken by weighing the dried samples before and after polymerization. Thermal gravimetric analysis (TGA) was carried out on DSC/TGA 1600 LF, METTLER TOLEDO instrument with a heating rate of $20^\circ \text{ C min}^{-1}$ under a nitrogen flow rate of 60 mL min^{-1} .

3. Results and discussion

3.1. Synthesis of functionalized GO by SI-ROMP

The main goal of this work is to investigate the feasibility of SI-ROMP from GO sheets. Due to various active oxygen-containing functional groups on GO sheets, Grubbs catalyst with high

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