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

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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, 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.

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
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), benzylidenenbis(tricyclohexylphosphine)dichloro-ruthenium (Grubbs 1st generation catalyst), (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(NBE), benzylidenebis(tricyclohexylphosphine)dichloro-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 (Et3N) (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 (CH2Cl2) (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 CH2Cl2 (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 CH2Cl2 and H2O 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 4000–400 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 CDCl3 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 Cu Kα source at room temperature. The data were collected from 5° to 60° at a scan rate of 15° 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 \[ \frac{m(\text{GO-PNb}) - m(\text{GO-NBE})}{m(\text{GO-NBE})} \times 100\% \], 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 °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
functional group tolerance is indispensable. Norbornene as a classical monomer of ROMP has been chosen. Our synthetic route to GO-PNb consists of four major steps (Scheme 1): (a) GO is synthesized from natural graphite powder by using modified Hummers’ method; (b) then GO is functionalized with excess 5-norbornene-2-acyl chloride to afford norbornenyl initiator ligands onto GO; (c) GO-NBE reacted with Grubbs catalyst to obtain effective GO-[Ru]; (d) chain growth polymerization of norbornene monomers is performed from GO sheets at room temperature.

FTIR spectroscopy as a facile characterization method was utilized to prove the synthetic process of GO-PNb (Fig. 1). Herein, GO was proved by the presence of several broad or intense absorption bands at 3400 cm\(^{-1}\) (the –OH groups stretching), 1720 cm\(^{-1}\) (the C=O stretching), 1400 cm\(^{-1}\) (the O–H deformation vibration), 1226 cm\(^{-1}\) (the C–O–H stretching) and 1050 cm\(^{-1}\) (the C–O–C stretching). The peak at 1620 cm\(^{-1}\) was assigned to C=C stretching of the un-oxidized graphitic domain on GO. After modification of GO sheets with norbornene, the peak at 2920 cm\(^{-1}\) (the C–H stretching) appeared, and that at 1720 cm\(^{-1}\) (the C=O stretching of esters) was strengthened, which reveals that norbornene was covalently linked to GO sheets. After the polymerization of norbornene, the characteristic peak at 967 cm\(^{-1}\) corresponding to trans-C=C from the PNb chains appeared. FTIR spectra analysis demonstrated that GO was successfully grafted with PNb chains by SI-ROMP.

Meanwhile, controlled experiments with the same reaction conditions by physically mixing GO and PNb or omitting the step of immobilizing catalysts for polymerization were carried out. FTIR spectroscopy indicated that there was no polymer grafted on GO, suggesting that PNb could not be physically absorbed onto GO and Grubbs catalyst is necessary to be linked on GO for ROMP.

The significant structural changes of the materials from graphite to GO-PNb during the modification process have been demonstrated by Raman spectra (Fig. 2). Graphite shows a prominent G band at 1580 cm\(^{-1}\) which originates from the primary in-plane vibrational mode, and a quite weak D band at 1334 cm\(^{-1}\), indicating that there are some inherent defects in the graphite we used \[58,59\]. After oxidation with KMnO\(_4\) and concentrated H\(_2\)SO\(_4\), GO shows two main features at 1598 cm\(^{-1}\) (G band) and 1352 cm\(^{-1}\) (D band) in its Raman spectrum. Compared with graphite, the D band

Scheme 1. Synthetic route to GO-PNb by SI-ROMP of norbornene and GO-ePNb with meta-chloroperoxybenzoic acid (MCPBA).
of GO becomes more prominent, which illustrates the reduction in size of the in-plane sp² domains and the increase of defects in plane [60], and the G band of GO becomes broadened and shifts from 1580 cm⁻¹ (graphite) to 1598 cm⁻¹. However, both the samples of GO-NBE and GO-PNb show two strong active Raman peaks, D band at 1352 cm⁻¹ and G band at 1600 cm⁻¹ where the G band also experiences a smaller red shift. These changes are caused by the defects in graphene sheets formed during the extensive oxidation and chemical functionalization. Generally, the intensity ratio of D and G bands (I_D/I_G) is the common metric that is used to characterize the defect density of graphene. For our samples, the I_D/I_G ratios of the GO, GO-NBE, and GO-PNb are 0.81, 0.94 and 0.98, respectively, reflecting the increase in disorder after functionalization with norbornene. The changes in the I_D/I_G ratio can be at least partly attributed to the covalent linkage between graphene and norbornene.

The solubility of GO in organic solvents was improved upon grafting with polymers. Prior to the functionalization, GO could be dispersed in water with long-term stability due to the presence of hydrophilic groups, whereas it is not dispersed in most organic solvents, such as CH₂Cl₂, chloroform (CHCl₃) and acetone [61].

Herein, the solubility of GO in organic solvents can be controlled by the nature of grafted polymers. Therefore, the samples of GO, GO-NBE and GO-PNb were dispersed in a mixed solvent of CH₂Cl₂/H₂O (v/v, 1/1) (Fig. 3). Due to the immiscible nature of CH₂Cl₂ and H₂O, the phase-separation happens with the CH₂Cl₂ phase at the bottom. As shown in Fig. 3, GO is completely dispersed in H₂O while GO-NBE and GO-PNb are completely dispersed in CH₂Cl₂. The obvious phenomenon demonstrated that the presence of norbornene makes the property of GO change from hydrophilic to hydrophobic. The conversion of solubility of GO in organic solvents also confirms the effectiveness of the covalent modification of GO. Fortunately, the level of solubility of GO-PNb is enough to use ¹H NMR spectroscopy to characterize the polymerized structures. The ¹H NMR spectra of PNb and GO-PNb (see Fig. S1) are nearly identical, revealing that norbornene monomers were successfully polymerized from the activated catalyst-functionalized GO.

The structure of graphite, GO, GO-NBE and GO-PNb were further investigated by powder XRD patterns (Fig. 4). Graphite exhibits a strong and sharp characteristic peak at 2θ = 26.6°, indicating a higher ordered structure, that corresponds to a basal spacing d₀₀₂ = 0.334 nm. Upon oxidation of graphite, the peak shifts to 11.12°, which indicates that the interlayer distance of GO increases to 0.794 nm. Compared to graphite (~0.334 nm), the increasing of the interlayer distance is attributed to the presence of oxygen-containing functional groups such as hydroxyl, carboxyl and epoxy groups. After functionalization of GO, the diffraction peak of GO-NBE shifts to lower angle, i.e., 2θ = 10.11°, corresponding to an interlayer distance of 0.874 nm. And the peak of GO-PNb further shifts to 9.488°, with an interlayer distance of 0.931 nm. The increase of interlayer distance during the chemical modification process reveals that ROMP has been carried out from GO successfully and GO-PNb remains an ordered layer structure with PNb intercalated between GO sheets under the chosen reaction conditions [35].

SEM was utilized to explore the morphology of GO-PNb composites (Fig. 5). The SEM images of GO shows wrinkled and layered structure due to the interactions between oxygen-containing functional groups. Prior to the functionalization, GO could be dispersed in water with long-term stability due to the presence of hydrophilic groups, whereas it is not dispersed in most organic
surfaces were covered with PNb. However, the coverage of PNb is low and non-uniform, resulting from the low grafting ratio of PNb.

3.2. Preliminary screening of polymerization conditions

As a new polymerization system on GO, the conditions of polymerization were analyzed by changing norbornene concentration, polymerization time and Grubbs catalysts. The grafting ratio of PNb on GO was calculated by gravimetry and the data was displayed in Table 1. The samples of GO-PNb01 to GO-PNb04 show the effect of norbornene concentration on the grafting ratio of PNb by using Grubbs 1st generation catalyst, suggesting that the grafting ratio of PNb is relatively low and irregular. Control experiments, where the lower monomer concentration \( \frac{C_i}{C_0} \) and \( \frac{C_1}{C_0} \) were used to repeat the polymerization with the same reaction conditions, demonstrated that there was no detectable information of PNb from GO by FTIR spectrum, and the grafting ratio was hard to be determined by gravimetry. In order to investigate whether norbornene could be utilized completely in polymerization or the degradation of PNb during the post-processing, the supernatant from the polymerization system was analyzed by FTIR spectroscopy. There were some norbornene left and no PNb could be detected. These results indicate that the conversion rate of norbornene during SI-ROMP on GO surfaces is low so that the grafting ratio is not high. We speculate that the unreacted oxygen-containing functional groups on GO sheets may have some influence on the activity of Grubbs 1st generation catalysts or even deactivate the catalysts in the polymerization process.

Grubbs 2nd generation catalyst was chosen for further research at the same reaction conditions because it provides a higher catalytic activity and better functional group tolerance than Grubbs 1st generation catalyst [48]. The results of GO-PNb05 to GO-PNb13 show that the grafting ratio of PNb became higher with an increase of norbornene concentration and/or polymerization time (Table 1). However, different from that with Grubbs 1st generation catalyst, the polymerization systems always became viscous at any reaction conditions. The viscous products, i.e., PNb, could be removed by repeated centrifugation and washing. The results of gravimetry show that the grafting ratio becomes appreciable although not very high (Table 1). Increased chain transfer from propagating polymer with the highly active Grubbs 2nd generation catalyst might be part of the reasons for the unexpected grafting ratio. The chain transfer includes intramolecular and intermolecular chain-transfer reactions [49]. In our case, secondary metathesis reactions on GO sheets happened during polymerization process (see Fig. S2) [39,62]. In an intramolecular chain-transfer reaction, self-metathesis with the active terminus of a PNb chain reacts with itself to release a polymer chain of reduced molecular weight and a cyclic macromolecule. In an intermolecular chain-transfer reaction, the reaction occurs on the same or different GO sheets. The PNb chain with active metal [Ru]alkylidene could react with any olefin at the backbone of a different PNb chain to form a macromolecule in reaction solution and a polymer chain on GO sheets. Therefore, the cross-metathesis on one GO sheet occurs and results in the formation of a cyclic polymer chain on GO sheet. And it forms a bridge polymer chain by crossing the different GO sheets. Collectively, these chain transfer reactions release many macromolecules from GO sheets, which decrease the grafting ratio of PNb. Because of the highly active Grubbs 2nd generation catalyst, the chain transfer reactions become much easier, leading to a viscous polymerization system.

The thermal stability and composition of GO-PNb were analyzed by TGA (see Fig. S3). From TGA curves (Fig. S3(f)), we found that GO was thermally unstable and it had 82 wt% weight loss between 50 °C and 700 °C. Compared with GO, the weight loss of PNb (Fig. S3(g)) was the pyrolysis of the polymer backbone at the temperature range from 400 °C to 550 °C. After grafting with norbornene (Fig. S3(e)) and PNb(Fig. S3(a–d)), smaller weight loss was found in the temperature below 210 °C, which indicated that the main oxygen-containing functional groups had been modified. The GO-PNb sample seems to have two main thermal events, one is oxygen-containing functional groups on GO, and the other is at higher temperature, resulting from the grafted PNb chains. These results illustrate that the higher grafting ratio of PNb on GO sheets is, the more distinct decomposition in TGA curves (between 400 °C and 550 °C).
XRD patterns of PNb grafted GO sheets using Grubbs 2nd generation catalyst were plotted in Fig. 6. After PNb was grafted on GO sheets, the characteristic diffraction peaks nearly at 10° shifted with increasing norbornene concentration and polymerization time, corresponding to the change of interlayer distance. All peaks shifted to nearly 9.0° with corresponding interlayer distance of 0.97 nm (Fig. 6A, from GO-PNb05 to GO-PNb08), and shifted to nearly 9.8° with the change of interlayer distance from ~0.87 nm to ~0.91 nm (Fig. 6B, from GO-PNb09 to GO-PNb13). Compared with GO-NBE (Fig. 4(c) interlayer distance of 0.87 nm), the interlayer distance of GO-PNb was increased after polymerization. It is found that the ordered layer structure still remained after SI-ROMP with norbornene from GO under the reaction conditions we chose. The grafted PNb intercalated among GO sheets to form an intercalated structure, which can be used for some potential applications such as electrochemical devices, adsorption of heavy metal ions and so on.

3.3. The epoxidation of the polymers on GO sheets

One of the specialty of ROMP is the functionality of double bonds in the backbone of resulting polymers, which allows for further chemical modification to yield desired functionalities, such as epoxide [63], sulfonate [63–65]. For further study of carbon double bonds along PNb chains, the epoxidation of GO-PNb was carried out (Scheme 1). Because of the improved solubility of GO-PNb in organic solvents, the GO-PNb was modified with MCPBA in CH2Cl2 to obtain the product of GO-ePNb at room temperature. The evidence of the epoxidation was illustrated by FTIR spectrum (Fig. 1). From the FTIR spectrum of GO-ePNb, it was found that the absorption of C=O–C stretching at 1078 cm⁻¹ became stronger than GO-PNb, and the absorptions of trans-C=C=O of PNb disappered. These two obvious characteristics could confirm that the epoxidation of GO-PNb occurred. Meanwhile, the peak at 1620 cm⁻¹ became smaller, attributing to the unoxidized graphitic domain where the C=C was partly epoxided by MCPBA. The GO-ePNb with many epoxy groups could also be used for further chemical functionalization to prepare novel and advanced GO/polymers composites.

4. Conclusions

In summary, GO has been successfully modified with PNb by SI-ROMP of norbornene and the double bonds along PNb chains can be epoxidized effectively. All the reactions were carried out under mild reaction conditions. The as-prepared GO-PNb is an intercalated layer structure with relatively low grafting ratio of polymers. And the improvement of solubility of polymerized materials in organic solvents such as CH2Cl2, CHCl3 and THF was realized, allowing for further chemical characterization and functionalization and creating convenient conditions for real applications. This work not only provides a novel general GO surface modification strategy, but also expands the application fields of SI-ROMP technique. Further studies involving the use of RGO as substrates to achieve controllable SI-ROMP and to establish structure–property relationship are currently underway in our laboratories.

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Appendix A. Supplementary data

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References


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