Chemical modification of graphene with a thermotropic liquid crystalline polymer and its reinforcement effect in the polymer matrix†

Ying Jing, Hui Tang,* Guijun Yu and Peiyi Wu*

In our work, graphene oxide (GO) was covalently functionalized with propargyl alcohol to obtain alkyne terminated graphene oxide. These alkyne groups on graphene oxide sheets further reacted with a kind of azido-functionalized liquid crystalline polymer via click chemistry, which was found to be a facile and effective method to graft the liquid crystalline polymer onto GO sheets. The liquid crystalline polymer introduced here was a side-chain liquid crystalline polymer – poly(2,5-bis[(4-methoxyphenyl)oxy]carbonyl styrene) (PMPCS). Azido-functionalized PMPCS was prepared beforehand by atom transfer polymerization to obtain polymers with designed molecular weight. The successful introduction of functional PMPCS chains onto GO sheets was confirmed by FTIR, TEM and AFM characterizations. Thermogravimetric analysis was used to calculate the graft efficiency. Raman and X-ray photoelectron spectroscopies revealed that functional PMPCS had more profound π–π stacking interactions and charge transfer effect with GO sheets after liquid crystalline phase transition. Therefore, the as-prepared GO–PMPCS composite had potential applications in improving the mechanical properties of liquid crystalline PMPCS matrix as had been investigated by rheological measurements.

1 Introduction

Intense interest in chemically modified graphene (CMG) has been aroused in the context of applications such as polymer composites, energy-related materials and biomedical applications due to its extraordinary electronic, thermal and mechanical properties. As compared with carbon nanotubes, nanoclay or other nanofillers, functionalized graphene nanomaterials have opened a wide window of applications due to their simpler synthesis procedure and efficient improvement in mechanical properties of polymers. Graphene oxide (GO), containing a range of reactive oxygen functional groups, which is easier to functionalize, has emerged as a precursor to bulk scale production of graphene-based materials. Different from fullerenes and carbon nanotubes, GO presents a two-dimensional flat structure with large specific surface area, which probably provides better interactions with modifying agents, especially when the modifying agents have large aromatic structures. Among the multitudinous graphene-based materials, GO–polymer composites form one large category. Various polymers such as polystyrene, PMMA, polyvinyl alcohol, polypropylene, polyurethane, polyester, and polycarbonate have already been applied as the polymer matrix in GO–polymer composites. The adoption of GO with more oxygen-containing groups, or graphene oxide grafted with the same polymer chains as the matrix, markedly improved the dispersion of the nanofiller within the polymer matrix.

So far, various chemical reactions that provide for either covalent or noncovalent attachment of polymers to the resulting CMG have been utilized to add functionality to groups present on the GO platelets. However, although the noncovalent modification method is simple to manipulate, it does not promote an exquisite combination of the participants. As for covalent modification, two important methodologies, grafting from and grafting to, are the most commonly employed. Compared with the grafting from method which does not provide a good control of polymer architecture, the grafting to method overcomes the former’s shortcomings by directly coupling the functional groups of polymer chains onto those of GO sheets. However, due to the difficulty in the molecular structure manipulation, although various covalent modification methods for GO have been developed, research relating to GO functionalized with well-defined polymers are still limited in the literature. In our previous works, click chemistry, one of the most important grafting to methods, has been successfully utilized to prepare PS-grafted GO and SEBS-grafted GO and realize the covalent modification of GO sheets with polymers of designed structures.
Although various polymers have been used to covalently or noncovalently modify GO, research concerning liquid crystalline polymers (LCPs) and GO composites have seldom been reported. However, much work remains to be done in enriching the functionalization of GO with LCPs, and discovery of special properties of the resultant composites have great significance both in theoretical and practical applications, since LCPs offer great opportunities in optical, thermal, electrical and mechanical applications. In the present study, fabrication of functional polymeric nanocomposites from thermotropic LCPs by incorporation of LCP-grafted GO was established. Here, poly(2,5-bis[4-methoxyphenyl]oxycarbonyl]styrene) (PMPCS), in which bulky aromatic side groups are connected to the backbones via covalent bonds, is introduced as the thermotropic LCP. It is noteworthy that, different from main-chain liquid crystalline polymers which are usually prepared by condensation polymerization with difficulty in controlling the MW, PMPCS, a typical class of side-chain liquid crystalline polymer, can be synthesized by radical polymerization which has the advantages of mild reaction conditions, lower purity requirements of materials, and easy MW control if controlled or “living” radical polymerization techniques are employed. Besides, the cooperative accommodation of laterally attached bulky aromatic side groups surrounding the extended backbone in PMPCS constructs the cylindrical building blocks, by which the polymers self-assemble into the columnar phases. Thus, the polymers may possess much more aromaticity in the ordered columnar phase than that in the amorphous state, which may afford better interactions with GO sheets.

Actually, similar to conventional end-on side-chain liquid crystalline polymers, many efforts have been devoted to develop the application of liquid crystalline polymers such as PMPCS in the fields of high modulus materials, nonlinear optics materials and other functional materials. However, previous works mainly focus on the structural design, synthesis and phase behavior investigation, and few mechanical properties optimization results have been reported. Therefore, to reinforce the mechanical properties of the polymer matrix, GO–PMPCS nanocomposites were synthesized and rheological measurements were conducted in this paper.

Herein, novel composites integrating chemically modified GO and PMPCS were prepared using the atom transfer radical polymerization (ATRP) method and “click” reaction. Then, the as-prepared GO–PMPCS composites were utilized to enhance the mechanical properties of PMPCS matrix which was investigated by rheological measurements. Interfacial interaction between the nanofillers and the matrix was evaluated in detail in order to gain insight into the improved mechanical properties.

2 Experimental section

2.1 Materials

Pristine graphite was purchased from Qingdao Huatai Graphite Co. (China). 2,5-Bis[4-methoxyphenyl]oxycarbonyl] styrene (MPCS) was synthesized according to the procedure reported previously. Cuprous bromide (CuBr) (Aladdin Reagent Co.) was dissolved in concentrated hydrochloric acid, precipitated in DI water, washed with ethanol and ethyl ether and dried under vacuum. N,N,N’,N”-pentamethyldiethylenetriamine (PMDETA, TCI, 99.5%) was used as purchased. Chlorobenzene (Sinopharm Chemical Reagent Co.), triethylamine (TEA) (Sinopharm Chemical Reagent Co.) and anisole (Aladdin Reagent Co.) were distilled over calcium hydroxide (Sinopharm Chemical Reagent Co.). 2,2′-Azo-bis(2-methylpropionitrile) (AIBN) (Aladdin Reagent Co.) was dissolved in acetone and recrystallized. Unless otherwise specified, all other reagents were purchased from commercial suppliers and used as received.

2.2 Instruments and measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus 470 spectrometer. Samples were prepared either as pellets using spectroscopic grade KBr as the diluent or as solution-cast films on pure KBr pellet. Samples for Raman characterization were directly deposited in powder form on glass sheets and the Raman spectra were collected on a Renishaw inVia Reflex micro-Raman spectrometer with 633 nm laser excitation. Molecular weight and polydispersity index (PDI, Mw/Mn) were determined by gel permeation chromatography (GPC) equipped with a G1362A refractive index detector. Tetrahydrofuran (THF) was employed as the eluent at a flow rate of 1.0 ml min⁻¹ at room temperature with monodispersed polystyrenes as standards. X-ray photoelectron spectroscopy (XPS) was performed with VARIOEL3 system. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Thermal Analyzer at a heating rate of 20 °C min⁻¹ under nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) patterns were recorded on Bruker D8 diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) images were taken with JEOLJEM-2100F microscope. Atomic force microscopy (AFM) images were obtained using Multimode Nano 4 in the tapping mode. For AFM observations, the samples were dispersed in acetone with the aid of sonication and then spin-coated onto freshly cleaved mica surfaces. Differential scanning calorimetry (DSC) analysis was performed on Mettler DSC-1 apparatus. All the experiments were carried out in a nitrogen atmosphere. Each sample weighed about 2–5 mg and was sealed in an aluminium pan. Data were based on the second heating process with a heating rate of 20 °C min⁻¹.

Rheological measurements were recorded on an ARES-9A rheometry instrument. Before tests, all the samples (PMPCS with different filler contents) were prepared into round discs with a diameter of 25 mm by compression molding at 130 °C. All the discs were vacuum dried overnight at 100 °C. When being tested, each disc was sandwiched between two circular plates. The plate distance was then adjusted to about 1 mm and the temperature was raised quickly to 130 °C. Samples were tested under a parallel plate mode with a controlled shear strain of 1% to ensure that all measurements were performed under linear viscoelastic region. Severe convecting nitrogen gas was used to protect the samples from oxidation during the rheological tests. Dynamic frequency sweeps were conducted from 0.1 to 100 rad s⁻¹ at different temperatures for each sample.
2.3 Preparation of azido-functionalized PMPCS

Azido-terminated PMPCS was prepared by ATRP procedure initiated with 3-azidoethyl-2-bromoisobutyrate (AEBiB). Two different molecular weight polymers, PMPCS (i) and PMPCS (ii) were prepared. For PMPCS (i), 0.4 g MPCs, 0.0115 g CuBr, 0.0136 g PMDETA, and 2.0 ml chlorobenzene were mixed in a dry Schlenk flask. For PMPCS (ii), 0.8 g MPCs, 0.0058 g CuBr, 0.0068 g PMDETA, 0.0094 g AEBiB, and 4.0 ml chlorobenzene were mixed in a dry Schlenk flask. After three freeze–pump–thaw cycles, the flask was sealed and the reaction proceeded at 90 °C for 24 h. The polymerization was quenched by liquid nitrogen and the polymer was precipitated in methanol for purification. Two different molecular weight polymers, PMPCS (i) and PMPCS (ii) were obtained. GPC results showed that PMPCS (i) had a molecular weight of 3200 g mol⁻¹ with polydispersity index of 1.07. PMPCS (ii) had a molecular weight of 11 400 g mol⁻¹ with polydispersity index of 1.08.

2.4 Preparation of terminal alkyne modified GO (tGO) sheets

GO sheets were synthesized from expandable graphite powders by a modified Hummers method and terminal alkyne modified graphene (tGO) sheets were synthesized according to the preparation procedure of terminal alkyne modified multi-wall carbon nanotubes. In a typical procedure, 140 mg GO sheets were refluxed in 40 ml SOCl₂ at 70 °C for 24 h with 0.5 ml DMF as the catalyst. After removing unreacted SOCl₂ by rotary evaporation, the remnant was vacuum dried at 40 °C for 24 h before dissolved in 140 ml DMF. A mixture of propargyl alcohol (0.28 g) and anhydrous TEA (8.1 ml) was added dropwise in an ice water bath under vigorous stirring. The mixture was stirred at 0 °C for another 1 h and then at 60 °C for 24 h. The collected powder was repeatedly rinsed with THF and water. After purification, the resulting powder was vacuum dried for 24 h at 45 °C, and tGO sheets were obtained.

2.5 Preparation process of GO–PMPCS composites via click chemistry

A 50 ml dry Schlenk flask was charged with 40 mg of tGO sheets, 0.123 g azido-functionalized PMPCS (i) or 0.373 g azido-functionalized PMPCS (ii) (the same molar amount as PMPCS (i)), 0.0024 g CuBr, 0.0028 g PMDETA, and 20 ml of DMF. After three freeze–pump–thaw cycles, the reaction proceeded at 90 °C for 24 h. As the cycloaddition reaction was accomplished, the mixture was dissolved in THF and filtered through a 220 nm PTFE membrane for five times to remove the impurities and unreacted PMPCS. The collected GO–PMPCS (i) and GO–PMPCS (ii) powders were then vacuum dried at 60 °C for 24 h.

2.6 Preparation of the PMPCS matrix by free radical polymerization

The PMPCS matrix was prepared by free radical polymerization. 5 g MPCs was dissolved in 50 ml anisole in a dry Schlenk flask. 0.0041 g AIBN was dissolved in 40 μl anisole and injected into the dry Schlenk flask. After three freeze–pump–thaw cycles, the reaction proceeded at 90 °C for 6 h. The polymerization was quenched by liquid nitrogen. Then 30 ml THF was added into the solution and the polymer was precipitated in methanol. The polymer was dissolved in THF and precipitated in methanol three times to remove the unreacted monomers. The obtained PMPCS was dried at 60 °C under vacuum for 24 h. GPC results showed that PMPCS matrix had a molecular weight of 97 000 g mol⁻¹, and the polydispersity index was 3.1.

2.7 Preparation of PMPCS matrixes with different GO–PMPCS composites contents

PMPCS matrixes with different GO–PMPCS composite contents were prepared by blending PMPCS matrix and the corresponding GO–PMPCS composite in THF. For each system, 0.4 g PMPCS matrix was adopted, and the filler weight proportions were 0.2 wt%, 0.7 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt% for GO–PMPCS (i) and GO–PMPCS (ii) respectively. After 2 h sonication, the filler was well dispersed in the solution. And then the solution was poured into methanol to obtain the loose solid blend. The solid blend was vacuum dried at 60 °C for 24 h.

3 Results and discussion

3.1 Grafting of PMPCS onto GO sheets

Preparation procedures of GO–PMPCS composites are illustrated in Scheme 1. Here, a click reaction, which has been utilized in the functionalization of carbon nanotubes and fullerenes was applied to PMPCS-grafted GO (GO–PMPCS composite) preparation. In our previous work, we have successfully prepared PS-grafted GO and SEBS-grafted GO. The detailed preparation process of azido-functionalized PMPCS (i) and PMPCS (ii) was shown in the experimental section. GPC results showed that PMPCS (i) had a molecular weight of 3200 g mol⁻¹, and its polydispersity index was 1.07. PMPCS (ii) had a molecular weight of 11 400 g mol⁻¹, and its polydispersity index was 1.08. FTIR spectra of PMPCS (i) and PMPCS (ii) were demonstrated in Fig. S1.† Obvious absorbance of azido groups in PMPCS (i) and PMPCS (ii) could be seen in the spectra.

The successful preparation of GO–PMPCS composites was confirmed by FTIR spectra as shown in Fig. 1. Due to the conjugated resonance of the triple bond in propargyl alcohol on the stretching vibration of carbonyl groups, red-shift of the stretching vibration of carbonyl groups on terminal alkyne modified GO (tGO) was observed after esterification with propargyl alcohol (the inset figure in Fig. 1 showed the magnification of the carbonyl stretching vibration region of GO and tGO). Additionally, new bands apparently arising from PMPCS characteristic for C–H stretching (3000–2800 cm⁻¹) and bending vibrations (1300–1100 cm⁻¹) of methyl and methylene groups were identified in the FTIR spectra of GO–PMPCS composites. However, the absorbance of azido groups could hardly be seen in GO–PMPCS composites due to their very small content.

Since the solubility of PMPCS and GO sheets is completely different in THF, the as-prepared GO–PMPCS composites were rinsed several times in THF to remove the unreacted PMPCS. Because PMPCS could form aggregates in acetone, the purified
GO–PMPCS composites were then dispersed in acetone and sample-prepared for TEM and AFM characterizations. A clear contrast between PMPCS and GO sheets was observed using TEM without staining as shown in Fig. 2(a) and (b). In our previous work, aggregates of dendritic-liner copolymer of PMPCS in acetone have also been observed and these vesicles were stable and retained their structures during solvent evaporation.

To better demonstrate the morphology of GO–PMPCS composites in acetone, AFM images (Fig. 2(c) and (d)) were taken to illustrate the surface state of the selected samples. The height of the aggregates was 40–50 nm in GO–PMPCS (i), and the height obviously became larger in GO–PMPCS (ii) (more than 50 nm) because of longer polymer chains. The aggregate sizes observed in this work were in accordance with those reported in our previous work, confirming that the nanospheres were indeed formed by PMPCS chains.

All the above FTIR, TEM and AFM characterizations demonstrated that azido-functionalized PMPCS were covalently grafted onto GO sheets in the two composites.

Thermogravimetric analysis as shown in Fig. 3 was carried out to calculate the graft efficiency of PMPCS onto GO sheets in the two composites. For pure GO and tGO, two major mass losses were identified which appeared around 100 °C and 200 °C, respectively. The former was attributed to the evaporation of adsorbed water and the latter was due to the decomposition of some oxygen-containing functional groups. Higher thermal stability was established for tGO sheets owing to the loss of some oxygen-containing groups during the acylation process. In addition to the mass loss of oxygen-containing groups of tGO, another obvious step of mass loss appeared around 300 °C and 700 °C for the two composites (Fig. 3(b) and (c)), which arose from the PMPCS chains grafted onto tGO sheets. The weight loss due to PMPCS decomposition in GO–PMPCS (i) composite was about 35 wt%. Considering the
molecular weight of 3200 g mol\(^{-1}\), the mass loss corresponded to functionalization of approximately one in 500 carbon atoms on graphene sheets. Although the same molar amount of PMPCS (i) and PMPCS (ii) were added during the click reaction, the graft efficiency of GO–PMPCS (i) was ten times that of GO–PMPCS (ii). However, the molecular weight of PMPCS (ii) was only three times that of PMPCS (i). Therefore, GO sheets were wrapped with more PMPCS chains in GO–PMPCS (i) than in GO–PMPCS (ii).

### 3.2 Investigation of the interactions between GO sheets and amorphous PMPCS/liquid crystalline PMPCS

It is worth noting that PMPCS is a typical MJLCP. The ordered structure of PMPCS in the liquid crystalline phase is strongly molecular weight dependent. When the \(M_n < 1.0 \times 10^4\) g mol\(^{-1}\), amorphous state was obtained regardless of the thermal history. When \(M_n > 1.6 \times 10^4\) g mol\(^{-1}\), hexagonal columnar nematic (\(\Phi_{hn}\)) phase with a \(d\)-spacing of 1.48 nm was formed. When \(1.0 \times 10^4 < M_n < 1.6 \times 10^4\) g mol\(^{-1}\), columnar nematic (\(\Phi_n\)) phase was formed with a \(d\)-spacing of 1.57 nm. Therefore, different from PMPCS (i), PMPCS (ii) with a molecular weight of 11 400 g mol\(^{-1}\) would form columnar nematic phase after liquid crystalline transition. The high density bulky side groups packing around the backbone offer opportunities for PMPCS (ii) to form \(\pi–\pi\) stacking interactions with GO sheets. After thermotropic liquid crystalline phase transition, the cooperative accommodation of the laterally attached bulky side groups surrounding the extended backbones constructs the cylindrical building blocks, by which PMPCS (ii) chains self-assemble into the columnar phases. Therefore, much more aromaticity was achieved for PMPCS (ii) in the ordered columnar phase than in the amorphous state and much better \(\pi–\pi\) stacking interactions with tGO sheets were formed after phase transition.

The above assumption was verified by Raman spectroscopy and X-ray photoelectron spectroscopy. Raman spectra of pure GO, tGO, GO–PMPCS (ii) at room temperature and at 170 °C were shown in Fig. 4. Two obvious bands located at around 1580 cm\(^{-1}\) and 1350 cm\(^{-1}\) were observed, which were generally assigned as the G band and D band, respectively. The G band is associated with the vibrations of sp\(^2\) carbon atoms in a graphitic 2D hexagonal lattice, while molecular weight of 3200 g mol\(^{-1}\), the mass loss corresponded to functionalization of approximately one in 500 carbon atoms on graphene sheets. The weight loss due to PMPCS decomposition in GO–PMPCS (ii) composite was only 15 wt%.

![Fig. 2 TEM images of GO–PMPCS (i) composite (a) and GO–PMPCS (ii) composite (b) dispersed in acetone and sample-prepared on copper grid. AFM images of GO–PMPCS (i) composite (c) and GO–PMPCS (ii) composite (d) dispersed in acetone and sample-prepared on mica flake.]

![Fig. 3 (a) TGA curves of GO, tGO, PMPCS (i), GO–PMPCS (i), PMPCS (ii) and GO–PMPCS (ii); (b) TGA and DTG curves of GO–PMPCS (i); (c) TGA and DTG curves of GO–PMPCS (ii).]

![Fig. 4 Raman spectra of pure GO, tGO, GO–PMPCS (ii) composite at room temperature and at 170 °C.]

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the D band is related to the vibrations of sp3 carbon atoms of defects and disorder.45 After modification with propargyl alcohol, the peak position of G band was of little change (1586 cm−1). However, the band red shifted partially to 1569 cm−1 in GO–PMPCS (ii) and graphitic “self-healing” effect was observed.46 The “self-healing” effect was ascribed to the influence of recovery from defects to ordered sp2 domains on GO sheets, which indicated that PMPCS had π–π stacking interactions with GO sheets and compensated some defects on GO sheets. Furthermore, the shift was more evident in GO–PMPCS (ii) at 170 °C.

On the other hand, the significant π-interactions between PMPCS (ii) molecules and graphene sheets were supposed to produce significant charge transfer effect.7,44–47 The electron withdrawal brought about by PMPCS (ii) changed the carrier concentration in tGO planes and caused the shift of Fermi level.7 The shift of sp2-peak (C=C) position in X-ray photoelectron spectra (Fig. 5) showed the shift of graphene Fermi level after grafting by PMPCS (ii).7 Compared with tGO (C–C 285.1 eV), a 0.6 eV downshift in GO–PMPCS (ii) was identified. After being heated, PMPCS (ii) went through thermotropic liquid crystalline transition, and the increased aromaticity promoted a more profound charge transfer in GO–PMPCS (ii) which caused another 0.2 eV downshift. The interactions between the tGO and PMPCS (ii) after phase transition are depicted in Scheme 2.

3.3 GO–PMPCS composites as fillers to improve the storage modulus of the PMPCS matrix

3.3.1 Dispersibility of the PMPCS matrix with GO–PMPCS composites in THF. GO–PMPCS composites could be used as fillers in the PMPCS matrix through solution blending because of the excellent compatibility of GO–PMPCS composites with PMPCS matrix in organic solvent. In the present work, the PMPCS matrix was prepared by free radical polymerization. GPC results showed that the PMPCS matrix had a number average molecular weight of 97 000 g mol−1, and the polydispersity index was 3.1. Fig. 6 showed the digital images of 0.3 g PMPCS matrices with different GO–PMPCS (i) contents dispersed in 2 ml THF. The digital images of the PMPCS matrices with different GO–PMPCS (ii) contents were nearly the same as GO–PMPCS (i) and were not shown. As a comparison, tGO was found to be poorly dispersed in THF.

3.3.2 Rheological properties of pure PMPCS matrix. Pure PMPCS matrix in THF solution was precipitated in methanol to obtain the solid PMPCS matrix. The solid was compression molded into a round disc with a fixed diameter of 25 mm at 130 °C. The round disc was used for parallel plate rheological measurements. The thickness of the round disc under test was controlled at 1 mm. Samples were tested under a parallel plate mode with a controlled shear strain of 1% to ensure that all measurements were performed under linear viscoelastic region. Severe convecting nitrogen gas was used to protect the samples from oxidation during the rheological tests. Dynamic frequency sweeps were conducted from 0.1 to 100 rad s−1 at different temperatures for each sample. From the frequency dependence of G′ for pure PMPCS shown in Fig. 7, obvious terminal behavior (G′ ~ ω^2) at lower frequency (ω = 0.1–1) and plateau region at higher frequency (ω = 10–100) due to chain entanglement were observed at 130 °C for PMPCS matrix, which were similar to many flexible chain polymers.48–50 At this temperature, PMPCS was in the amorphous state. When the temperature rose to 140 °C, slight terminal behavior was observed at this stage but the plateau region disappeared due to the increasing rigidity and reduction in entanglement of the polymer chains. According to our previous work,51 the formation of the liquid crystalline phase of PMPCS depended on the adjustment between the main chains and the side groups. Before 140 °C, the side chains responded faster to the temperature, but the main chains still remained unmoved. At this stage, the mesophase formation had already proceeded, but was not complete. Therefore, an unstable mesophase was developed at this stage. However, when the temperature reached 150 °C,
the rheological properties of these nanocomposites were studied. Like pure PMPCS, all PMPCS matrix/GO–PMPCS nanocomposites were compression molded into round discs with a fixed diameter of 25 mm at 130 °C. The thickness of the round discs under test was controlled at 1 mm. Detailed results of the angular frequency dependence of storage modulus at various temperatures were shown in Fig. S2.† To make it simple, four representative angular frequencies (0.1, 1.0, 10 and 100 rad s⁻¹) were chosen instead of the whole frequency range.

The storage modulus of the PMPCS matrices with different GO–PMPCS composite contents at 130 °C was shown in Fig. 8. The storage modulus of PMPCS matrix with GO–PMPCS (i) first decreased with increasing filler content, and then increased again at 1.0 wt% filler content. For the PMPCS matrix with GO–PMPCS (ii), the storage modulus also decreased first with increasing filler content, but increased again at 1.5 wt% filler content.

At 130 °C, PMPCS matrix was in the amorphous state. In the amorphous state of the PMPCS matrix, the decrease of storage modulus was due to the less compaction of the PMPCS matrix after a small amount of filler addition. However, with increasing the filler content, the storage modulus increased again due to the reinforcement effect.

At 140 °C, 0.2 wt% the content of both GO–PMPCS composites showed little improvement in the storage modulus of PMPCS matrix. However, better improvement in the storage modulus of the matrix was identified at 0.7 wt%, 1.0 wt% and 1.5 wt% filler content. When the GO–PMPCS composite content was increased to 2.0 wt%, the storage modulus of the matrix was greatly improved, and the exact enlargement factors at different angular frequencies compared with pure PMPCS matrix were shown in Fig. 9(a) and (b). At the low frequency of 0.1 rad s⁻¹, the enlargement factor was nearly the same for both GO–PMPCS composites (both 2.6). At higher frequencies 1.0 rad s⁻¹ and 10 rad s⁻¹, the enlargement factors with GO–PMPCS (i) (1.0 rad s⁻¹ 3.7, 10 rad s⁻¹ 3.2) became obviously larger than those with GO–PMPCS (ii) (1.0 rad s⁻¹ 2.2, 10 rad s⁻¹ 2.0), indicating that GO–PMPCS (ii) had better improvement effect than GO–PMPCS (i). However, at even higher frequencies 100 rad s⁻¹, the enlargement factors become close again (GO–PMPCS (i) 1.9, GO–PMPCS (ii) 1.8). This was because at 140 °C, the PMPCS matrix was in an unstable mesophase, and the high shear rate would reduce the reinforcement effect of the fillers.

![Digital images of 0.3 g PMPCS matrices with different GO–PMPCS contents dissolved in 2 ml THF (a) pure PMPCS matrix, (b) 0.2 wt%, (c) 0.7 wt%, (d) 1.0 wt%, (e) 1.5 wt%, (f) 2.0 wt%, and (g) PMPCS matrix with 1.0 wt% tGO.](image1)

**Fig. 6** Digital images of 0.3 g PMPCS matrices with different GO–PMPCS contents dissolved in 2 ml THF (a) pure PMPCS matrix, (b) 0.2 wt%, (c) 0.7 wt%, (d) 1.0 wt%, (e) 1.5 wt%, (f) 2.0 wt%, and (g) PMPCS matrix with 1.0 wt% tGO.

![Frequency dependence of $G'$ for pure PMPCS matrix at various temperatures.](image2)

**Fig. 7** Frequency dependence of $G'$ for pure PMPCS matrix at various temperatures.

not only the side chains but also the main chains involved in the phase transition process. The mesophase formation tended to complete at 150 °C and higher, and this stage was defined as the stable mesophase. In the present study, no terminal behavior ($G' \sim \omega^2$) at lower frequency ($\omega = 0.1$–1) could be observed with the temperature rising to 150 °C and the dependence of storage modulus on frequency became weak, indicating the formation of a stable mesophase. The dependence of the storage modulus on frequency at 160 °C and 170 °C was similar to that at 150 °C, confirming the fact that PMPCS had entered a stable mesophase stage at 150 °C.

Notably, the storage modulus of the PMPCS matrix in the amorphous state was much higher than that in the mesophase, which could be explained by the model put forward by Kornfield. In her opinion, the decrease in storage modulus of side-chain liquid crystalline polymers during the isotropic-nematic transition could be attributed to a tube dilation associated with enhanced mesogen mobility.

### 3.3.3 Rheological properties of PMPCS matrix/GO–PMPCS nanocomposites

The large decrease of the storage modulus of PMPCS matrix during the liquid crystalline phase transition greatly hindered the application of the material. In this context, GO–PMPCS composites which had excellent compatibility with the PMPCS matrix were used as a reinforcing agent. PMPCS matrices with different GO–PMPCS composites contents 0.2 wt %, 0.7 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt% were prepared, and the rheological properties of these nanocomposites were studied. Like pure PMPCS, all PMPCS matrix/GO–PMPCS nanocomposites were compression molded into round discs with a fixed diameter of 25 mm at 130 °C. The thickness of the round discs under test was controlled at 1 mm. Detailed results of the angular frequency dependence of storage modulus at various temperatures were shown in Fig. S2.† To make it simple, four representative angular frequencies (0.1, 1.0, 10 and 100 rad s⁻¹) were chosen instead of the whole frequency range.

![Storage modulus of PMPCS matrix with (a) different GO–PMPCS (i) contents and (b) different GO–PMPCS (ii) contents at 0.1, 1.0, 10 and 100 rad s⁻¹ angular frequency at 130 °C.](image3)

**Fig. 8** Storage modulus of PMPCS matrix with (a) different GO–PMPCS (i) contents and (b) different GO–PMPCS (ii) contents at 0.1, 1.0, 10 and 100 rad s⁻¹ angular frequency at 130 °C.
At 150 °C, the PMPCS matrix entered a stable mesophase. The highest improvement effect at this temperature was also found at 2.0 wt% filler content. Additionally, better improvement effect was obtained with GO–PMPCS (i) at any angular frequency compared with GO–PMPCS (ii) and the corresponding enlargement factors were shown in Fig. 10(a) and (b). For GO–PMPCS (i), the enlargement factors were 3.8, 5.0, 5.0 and 6.2 for 0.1 rad s\(^{-1}\), 1.0 rad s\(^{-1}\), 10 rad s\(^{-1}\) and 100 rad s\(^{-1}\), respectively. For GO–PMPCS (ii), the enlargement factors were 2.2, 2.4, 2.4 and 2.9 for 0.1 rad s\(^{-1}\), 1.0 rad s\(^{-1}\), 10 rad s\(^{-1}\) and 100 rad s\(^{-1}\), respectively.

It could be noted that both GO–PMPCS composites had better improvement effect in the mesophase state (140 °C and 150 °C) of PMPCS matrix than in the amorphous state (130 °C). As had already been investigated above, tGO sheets interacted better with mesomorphic PMPCS chains by π-π stacking interactions and charge transfer effect.

Furthermore, a better improvement effect in storage modulus was obtained for GO–PMPCS (i) in the mesophase than GO–PMPCS (ii). This was attributed to the higher graft efficiency of PMPCS onto tGO sheets in GO–PMPCS (i) as revealed by TGA results. The functionalization of PMPCS (i) was approximately one in 500 carbon atoms on graphene sheets, and the functionalization of PMPCS (ii) was only one in 5000 carbon atoms on graphene sheets. Therefore, GO–PMPCS (i) was wrapped by more PMPCS chains and had better compatibility with PMPCS matrix. This better compatibility played an important role in enhancing the storage modulus.

3.4 Mesomorphic structure and thermal behavior of PMPCS matrices with different GO–PMPCS composite contents

The mesomorphic structure of the above mentioned PMPCS matrices with different GO–PMPCS composites was studied using wide-angle X-ray diffraction and the results were shown in Fig. S3.† Although the mesophases of PMPCS were found to be stable up to the decomposition temperature of the samples (350 °C), PMPCS matrices with different GO composites contents were measured by heating up to 170 °C since higher temperatures would cause the decomposition of the oxygen containing groups on the GO sheets. All the samples for X-ray diffraction were directly obtained from the samples used in the rheological measurements above. After quenched to room temperature from 170 °C, a narrow diffraction peak at 2θ = 5.7° (d-spacing of 1.48 nm), corresponding to hexagonal columnar nematic (H\(_{\text{I}}\)) structure could be observed with different GO–PMPCS composites contents. Generally, the incorporation of two kinds of GO–PMPCS composites with contents from 0.2 wt% to 2.0 wt% did not disrupt the mesomorphic structure of the PMPCS matrix.

The thermal behavior of the PMPCS matrix with different GO–PMPCS composite contents was investigated by differential scanning calorimetry (DSC) and the results are shown in Fig. S4.‡ For conventional thermotropic liquid crystals, the general phase transition process involves: crystalline state → liquid crystalline state → isotropic state. However, PMPCS is noncrystalline or amorphous before liquid crystalline phase transition, and no endothermic peak correlative to any melting point of crystals can be identified. It is speculated that the bulky substituents along the polymer chains hinder the crystallization of the polymer.53 Meanwhile, the liquid crystalline phase transition of PMPCS cannot be detected by DSC. Only the glass transition temperature of PMPCS can be observed during the entire thermal process.42 Since the thermal event associated with order–disorder transition cannot be detected by DSC, it is possible that the transition possess a dominant entropy change which attributed to a supramolecular structure change.54 Second heating DSC thermal diagrams (20 °C min\(^{-1}\) heating rate) were discussed here since the previous thermal histories of the samples were erased. The thermogram was featureless except the glass transition at 116 °C. Because neither of the two GO–PMPCS composites showed any features in the DSC curves in the whole temperature range (not shown), the thermograms of PMPCS matrix with GO–PMPCS composites (2.0 wt%) only showed the glass transition of PMPCS. It could be seen that the glass transition temperature remained the same in PMPCS matrix with 2.0 wt% GO–PMPCS (i) and 2.0 wt% GO–PMPCS (ii). It was worth noting that the addition of GO–PMPCS composites, even in 2.0 wt% content, did not change the glass transition temperature of PMPCS.

4 Conclusions

Functionalized GO sheets with a kind of thermotropic liquid crystalline polymer—PMPCS were successfully prepared via ATRP and click chemistry in our work. Because the liquid
crystalline phase transition of PMPCS is strongly molecular weight dependent, two different molecular-weight PMPCS molecules were designed. The smaller molecular weight PMPCS (i) remained amorphous after being heated, but the larger molecular weight PMPCS (ii) could go through a thermotropic liquid crystalline transition after being heated. Thermogravimetric analysis of the two kinds of GO–PMPCS composites showed that PMPCS (i) had much higher graft efficiency onto GO sheets than PMPCS (ii).

Interestingly, further Raman and XPS study found that liquid crystalline PMPCS (ii) had better interactions with GO sheets than its amorphous state. This could be ascribed to the fact that the increased aromaticity of PMPCS (ii) had better interactions with GO sheets than PMPCS (i).

What's more, the as-prepared GO–PMPCS composites had much better compatibility with PMPCS matrix compared with pure GO sheets. The composites could be used as nanofillers for PMPCS matrix by a facile solution blending method and the PMPCS matrix by a facile solution blending method and the following precipitation process. Rheological measurements showed that the storage modulus of PMPCS matrix at the mesophase state improved a lot with very small nanofiller contents. GO–PMPCS (i) with higher graft efficiency had a better reinforcement effect than GO–PMPCS (ii) at the same filler content, due to the former’s better compatibility.

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Notes and references