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Solubilization of Graphene Flakes Through Covalent Modification with Well-Defined Azido-Terminated Poly(ε-caprolactone)

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ABSTRACT: A well-defined poly(ε-caprolactone) (PCL) with terminal azido group was prepared. Grafting-on reaction between the azido-terminated PCL (N_3—PCL) and ultrasonication-assisted exfoliated graphene flakes (GF) was carried out to obtain PCL-grafted-GF (PCL-*g*-GF) which showed good dispersibility in a wide variety of organic solvents. Gel permeation chromatography, ^{1}H NMR, IR, Raman, UV-vis, and TEM measurements indicated that PCL macromolecules were covalently introduced on the surface of GF without disrupting the structure of GF. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41569.

KEYWORDS: composites; graphene and fullerenes; ring-opening polymerization

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INTRODUCTION

Since the discovery of graphene by Geim and coworkers in 2004,[1] graphene has attracted widespread attention due to its unique properties, such as high surface area, excellent thermal and electrical conductivities, and strong mechanical strength.[2–5] Graphene-based nanomaterials have many promising applications in energy-related and environmental-related areas. For instance, in energy-related areas, modified graphene materials have been used in photovoltaic cells,[6,7] lithium ion batteries,[8,9] supercapacitors,[10] and fuel cells.[11] In the environmental remediation area, some graphene-based materials have been used for the degradation of toxic organic pollutants and as sensor devices for pollutant analysis.[12,13] However, the limited solubility of graphene due to the strong π–π interaction limits the exertion of its great potentials. Materials with solution processability and good film-forming property have a number of applications for low-cost device fabrications.

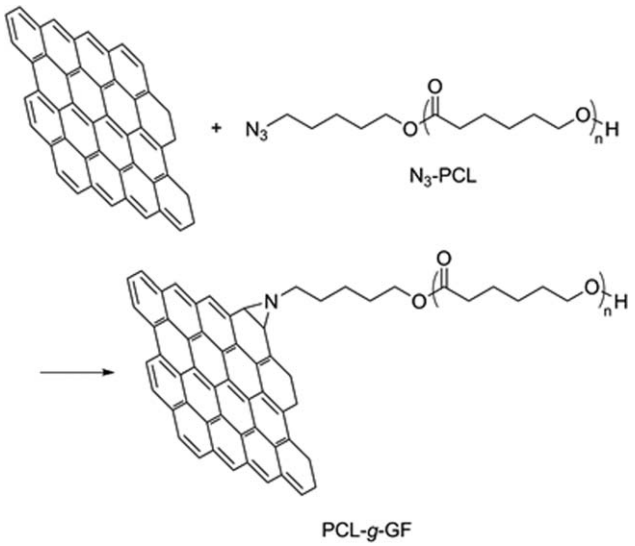
Various efforts have been made to prepare soluble graphene/polymer composites by modification of graphene with organic polymers.[14–16] We are interested in poly(ε-caprolactone) (PCL) as a polymer segment for a graphene/polymer composite. As PCL is a biodegradable and biocompatible polyester with a number of potential applications, PCL-functionalized graphene is expected to find use in biomedical materials, biomedical engineering, biosensor, and materials for drug delivery system. To the best of our knowledge, most of the covalent modification of graphene with PCL reported in the literatures are based on grafting-from method using graphene oxide (GO) as a starting material.[17–19] The grafting-from modification involves two reaction steps composed of introduction of OH groups onto GO surface, followed by *in situ* ring-opening polymerization of ε-caprolactone (CL). Such prepared PCL-functionalized GO may contain some defect structures arising from multistep reactions (oxidation, hydrolysis, and ring-opening polymerization). Further, it is necessary to reduce GO to graphene-like sheets by removing the oxygen-containing groups to restore a conjugated structure.

In this work, we examined one-step functionalization of exfoliated graphene flakes (GF) with preformed azido-terminated PCL (N_3—PCL) to obtain PCL-grafted-GF (PCL-*g*-GF) as shown in Scheme 1. This method does not need restoration of graphene from GO. The key reaction is nitrene chemistry to introduce PCL macromolecules on GF. The thermally generated nitrene radicals from azido groups possess high reactivity and can attack the double bonds in carbon nanomaterials, such as fullerenes, carbon nanotubes, and graphenes to form the covalent bonds of C—N.[20–22]

EXPERIMENTAL

Materials

Graphite nanoplatelets (GNP) (nominal average size, 5 μm; thickness, 5–10 nm) were purchased from XG Sciences, USA. 5-Azido-1-pentanol was prepared according to the reported procedure.[23] ε-Caprolactone (CL) (Tokyo Kasei Kogyo, Japan) was



Scheme 1. Grafting-on Functionalization of GF with N_3—PCL.

distilled over CaH_2 under reduced pressure. All other reagents were purchased from commercial sources and purified by conventional method.

Measurements

^1H NMR spectra were recorded at room temperature on a JEOL α-500 nuclear magnetic resonance spectrometer. Samples were dissolved in $CDCl_3$ and tetramethylsilane (TMS) was used as the internal standard. Infrared and UV-vis spectra were recorded on a JASCO FTIR-4100 and Shimadzu UV-2550, respectively. Thermogravimetric analysis (TGA) was performed with SII EXSTER-6000 under N_2 gas flow. The heating range was extended from 30 to 1000°C, and the heating rate was 10°C/min. Gel permeation chromatography (GPC) was carried out on a Tosoh HLC-8020 chromatograph equipped with a set of polystyrene gel columns (Tosoh TSK gel G2500H + G3000H) and refractive/ultraviolet dual mode detectors. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. The calibration curves for GPC analysis were obtained using polystyrene standards. Matrix-assisted laser desorption/ionization-time-of-flight-mass spectroscopy (MALDI-TOF MS) was performed with a Shimadzu Kompact II spectrometer in the linear mode with an acceleration voltage of 20 kV. The sample solution was prepared by the dissolution of polymer (1 mg) in 1 mL of THF. The matrix solution was prepared by the dissolution of α-cyano-4-hydroxycinnamic acid (23 mg) in 1 mL of THF. Matrix and polymer solutions were mixed in a 1 : 1 ratio. To aid sample ionization, the MALDI target was prespotted with 0.5 μL of a 0.1 mmol/mL solution of silver sodium iodide in THF and allowed to dry at room temperature. A 0.5–1.0 μL aliquot of the polymer/matrix mixture was deposited on top of ionization agent and air-dried. The morphology of the GF was observed using a HITACHI H-800 transmission electron microscope operated at 100 kV. Raman spectra were recorded on a Horiba XploRa with an excitation wavelength of 638 nm and a beam spot size of 1–2 μm.

Preparation of N_3—PCL

Into a solution of 5-azido-1-pentanol (0.20 g and 1.6 mmol) and CL (4.4 g and 39 mmol) in 15 mL of toluene was added diphenyl phosphate (0.40 g and 1.6 mmol) in a glove box. The reaction mixture was stirred under an argon atmosphere for 5 h at room temperature. The polymerization was quenched by the addition of Amberlyst A21. The polymer was isolated by precipitation in cold methanol/hexane. The obtained polymer was further purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (2 : 1 by volume) to give 3.0 g (65%) of N_3—PCL as a white solid. M_n (NMR) = 2500; M_n (GPC) = 3270; M_w/M_n (GPC) = 1.5; IR (KBr): ν = 2945 (s), 2866 (s), 2100 (w), 1728 (s), 1186 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$, δ): 4.06 (t, J = 5.8 Hz), 3.66 (t, J = 6.4 Hz), 3.29 (t, J = 6.8 Hz), 2.31 (t, J = 6.4 Hz), 1.7–1.6 (m), 1.4–1.3 (m).

Preparation of Ultrasonication-Assisted Exfoliated Graphene Flakes

GNP (50 mg) was added into a sonication glass tube that contained 50 mL of N-methylpyrrolidone (NMP). The dispersion was deoxygenated for 30 min by bubbling with N_2 and ultrasonicated using the bath ultrasonic processor at 11 ± 1°C running at 310 W for 300 min. After sonication, 50 mL ethanol was added to the reaction mixture, and the mixture was centrifuged for 1 h at 5000 rpm. The resulting sediment was dried at 100°C for 1 h to remove ethanol. Exfoliated GF was obtained as black sediment (45 mg).

Preparation of PCL-Grafted Graphene Flakes

A mixture of exfoliated GF (20 mg), N_3—PCL (20 mg) and NMP (10 mL) was stirred thoroughly for 15 min under nitrogen bubbling and heated at 160°C for 24 h under nitrogen atmosphere. When the reaction was finished, the reaction mixture was cooled to room temperature. After centrifugation (1000 rpm, 30 min) to remove unreacted GF, the supernatant was filtered with TEFLON filter (0.45 μm) and poured into diisopropyl ether (IPE) to precipitate crude PCL-*g*-GF. The crude product was then dispersed in ether and the mixture was centrifuged for 20 min at 3000 rpm. Purified PCL-*g*-GF was obtained after freeze-drying as a dark brown solid (22 mg). M_n (GPC) =12000; M_w/M_n (GPC) = 1.3; IR (KBr): ν = 2946 (s), 2864 (s) 1730 (s), 1185 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$, δ): 4.06 (t, J = 5.8 Hz), 3.66 (t, J = 6.4 Hz), 3.6–3.4, 2.31 (t, J = 6.4 Hz), 1.7–1.6 (m), 1.4–1.3 (m).

RESULTS AND DISCUSSION

Preparation of N_3—PCL

We are interested in one-step covalent modification of GF with PCL using grafting-on method. Among various chemical reactions for attaching polymers onto graphene, nitrene chemistry is considered to be a useful means to covalently modify graphene and other nanocarbons because only nitrogen molecule generates as a by-product. We prepared a well-defined N_3—PCL via the controlled/living ring-opening polymerization of CL with diphenyl phosphate as an efficient organocatalyst developed by Kakuchi and coworkers.[24] The degree of polymerization was designed to be around 20. These relatively short polymer chains should be sufficient to control the solubility of the attached GF. Moreover, the low molecular weight simplifies the characterizations such as IR, NMR, and MALDI-TOF MS analysis.

Figure 1 shows MALDI-TOF MS of N_3—PCL used in this study. MALDI-TOF MS is one of the most accurate methods available

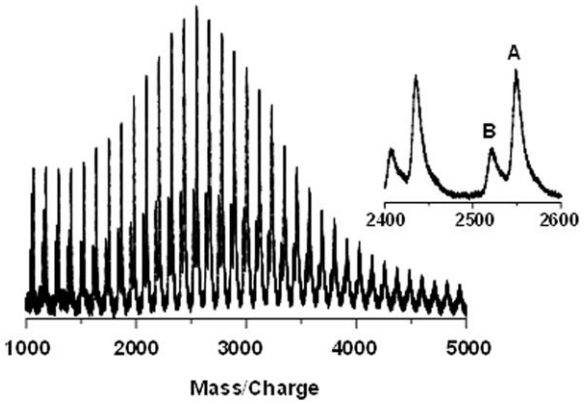


Figure 1. MALDI-TOF MS of N_3—PCL.

for end group identification in polymer. Two series A and B were observed in the spectrum. The major peak series A can be assigned to the sodium adducts of N_3—PCL. The mass/charge ratio for the major series A is expressed by the following formula: $m/z = 23 + 129 + 114n$, where n is the degree of polymerization. The molecular weight of the minor peak series B was smaller than that of A by 28 Da which corresponds to the molecular weight of nitrogen. This indicates the fragmentation of the azido groups via expulsion of N_2 during MALDI process.[25]

Preparation of Ultrasonication-Assisted Exfoliated Graphene Flakes

Liquid-phase exfoliation of graphene with the aid of ultrasonication is a convenient method because large-scale production of exfoliated graphene is possible. Khan et al. reported solvent-exfoliated graphene at extremely high concentration in NMP.[26] Shen et al. carried out ultrasonication of pristine graphene in an aqueous PVA solution.[27] PVA macroradicals generated during sonochemical degradation of the PVA solution can be bound to graphene surface to prevent restacking. Thus, our first attempt to introduce PCL macromolecules onto GF was ultrasonication treatment of GNP in the presence of N_3—PCL. However, we found PCL underwent severe decomposition during ultrasonication process to obtain complex reaction products. Alternatively, grafting-on reaction was carried out by the reaction of N_3—PCL with the isolated ultrasonication-assisted exfoliated GF. We prepared GF by ultrasonication-assisted exfoliation of GNP according to our previously reported procedure.[9]

Grafting-On Reaction

Grafting of PCL macromolecules onto GF was carried out by heating the mixture of GF and N_3—PCL in NMP at 160°C under nitrogen atmosphere. The crude product was obtained by precipitation into IPE. To remove unreacted N_3—PCL, the crude product was then precipitated in ether. Purified PCL-*g*-GF was obtained as the sediment after centrifugation as a dark brown solid.

Characterization of PCL-g-GF

Figure 2 shows GPC traces of N_3-PCL and PCL-*g*-GF. PCL-*g*-GF showed a unimodal GPC curve that shifted from 3000 to 12,000 after grafting reaction. This increase of molecular weight

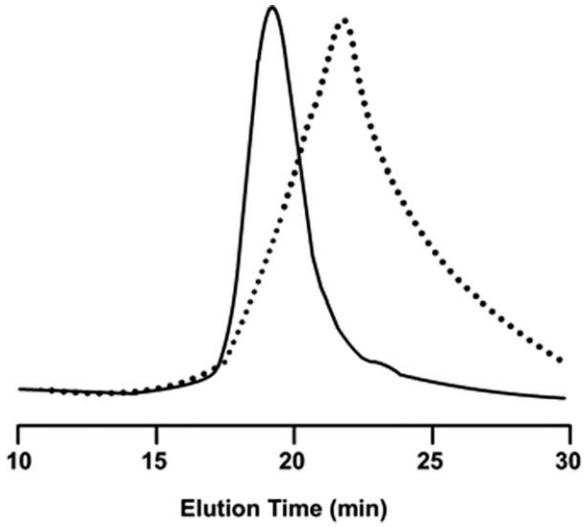


Figure 2. GPC traces of N_3—PCL (dotted line) and PCL-*g*-GF (solid line).

can be explained by the attachment of PCL chains onto GF. The GPC curve of PCL-*g*-GF did not contain low molecular weight fraction, indicating that PCL-*g*-GF was obtained without contamination of unreacted N_3—PCL. The reason for the narrower molecular weight distribution of PCL-*g*-GF than that of N_3—PCL may be fractionation during repeated precipitation process.

Figure 3 shows ^{1}H NMR spectra of N_3—PCL and PCL-*g*-GF in $CDCl_3$. In addition to absorptions due to PCL main chains, small absorptions due to the terminal moieties at α- and ω-ends are clearly observed. The peaks at 3.7 (peak a) and 3.3 (peak b) ppm are due to methylene protons of —CH_2—OH and —CH_2—N_3, respectively [Figure 3(a)]. After reaction with GF, the peak at 3.3 ppm due to methylene protons next to azido groups disappeared completely. Conversely, the methylene protons next to terminal hydroxy group remained [Figure 3(b)].

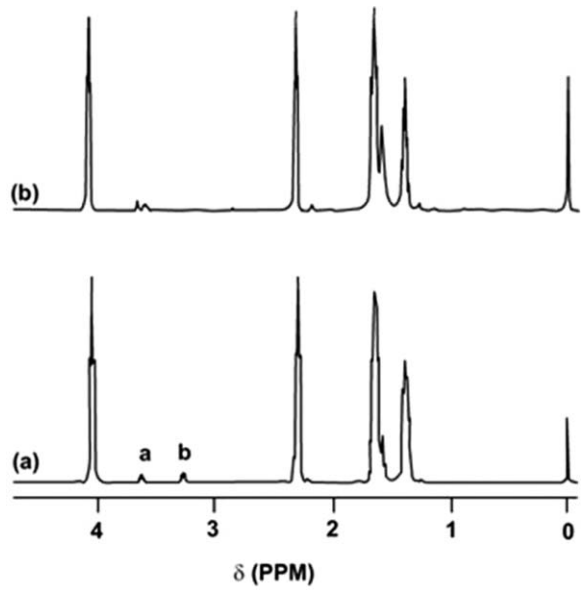


Figure 3. ^{1}H NMR spectra of (a) N_3—PCL and (b) PCL-*g*-GF.

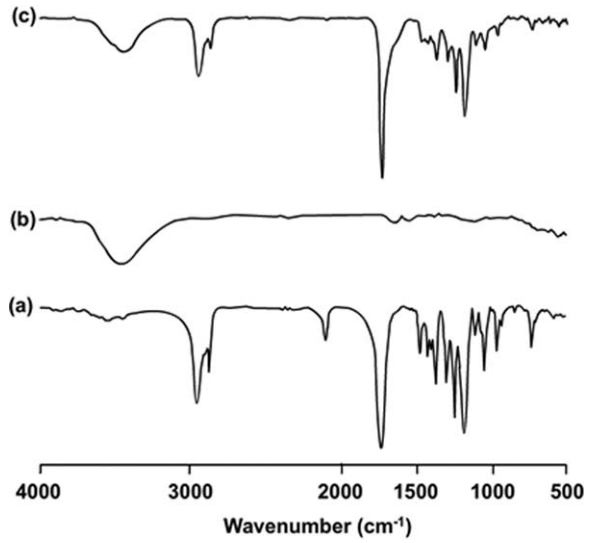


Figure 4. IR spectra of (a) N_3—PCL, (b) GF, and (c) PCL-*g*-GF.

These observations indicated successful introduction of PCL chains onto GF.

Figure 4 shows IR spectra of PCL-*g*-GF, N_3—PCL, and GF. N_3—PCL exhibited a characteristic absorption peak at 2100 cm^{-1} due to the azide groups [Figure 4(a)]. GF do not possess any characteristic fingerprint modes in the absorption spectrum [Figure 4(b)]. After reaction with N_3—PCL, characteristic absorption peaks due to PCL moiety were clearly observed at 2946 (ν_{C-H}), 2864 (ν_{C-H}), 1730 ($\nu_{C=O}$), and 1185 cm^{-1} (ν_{C-O}). Conversely, the absorption at 2100 cm^{-1} due to azido groups disappeared completely, indicating the complete conversion of azido precursor to nitrene [Figure 4(c)].

The successful grafting of PCL macromolecules onto GF was also confirmed by Raman spectra in the region 1200–2000 cm^{-1} as shown in Figure 5. The spectrum of GF was composed of D (1355 cm^{-1}) and G (1580 cm^{-1}) bands, similar to the Raman spectrum of high-quality GF obtained from liquid phase exfoliation of graphite.[28,29] Apparently, these two peaks

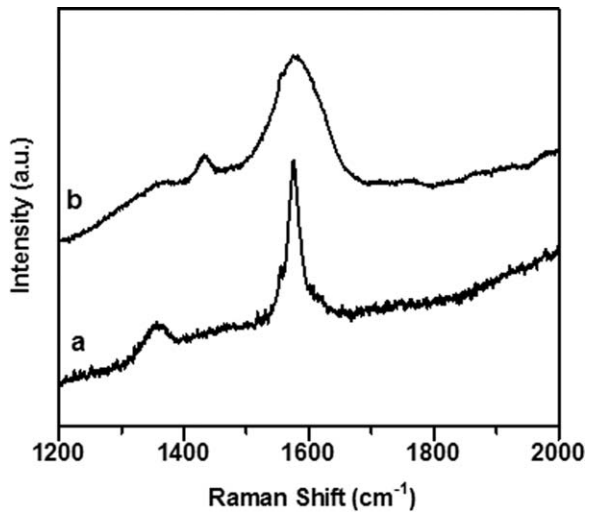


Figure 5. Raman spectra of (a) GF and (b) PCL-g-GF.

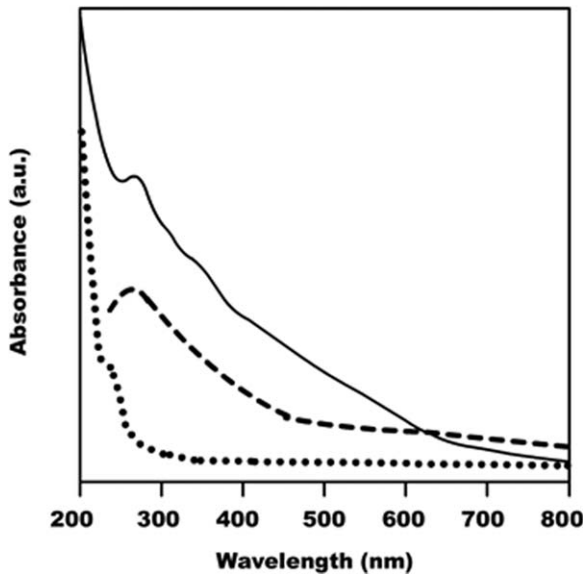


Figure 6. UV-vis spectra of N_3—PCL in CH_3CN (dotted line), GF (dashed line), and thin film of PCL-*g*-GF (solid line).

were broadened in the spectrum of PCL-*g*-GF. This peak broadening is probably associated with some structural changes in sp^2 conjugated carbon due to covalent bond formation with PCL macromolecules. It should be noted that new peak emerged at 1430 cm^{-1} after functionalization. This peak can be assigned to PCL introduced on GF because Raman spectrum of PCL is reported to exhibit a strong peak at 1430 cm^{-1}.[30,31]

To check the retention of π-conjugated structure of GF after functionalization, we examined UV-vis absorption spectra of PCL-*g*-GF, N_3—PCL, and GF as shown in Figure 6. N_3—PCL showed strong absorption in the wavelength region shorter than 250 nm, while no evident absorption in the longer wavelength. GF showed a peak centered at 270 nm with continuously decreasing intensity. It is known that UV-vis spectrum of reduced GO exhibits absorption at 270 nm due to the restoration of electronic conjugation.[32] The absorption of PCL-*g*-GF was characteristic of both N_3—PCL and GF. The existence of the peak at 270 nm in PCL-*g*-GF indicated the retention of electronic conjugation structure of GF after grafting-on reaction.

The relative amounts of the grafted PCL macromolecules on GF were determined by TGA analysis. Figure 7 shows the TGA thermograms of GF, N_3—PCL, and PCL-*g*-GF under nitrogen atmosphere at the heating rate of 10 K/min. The overall weight loss of GF was about 8% at 1000°C, showing its good thermal stability (dashed line). In the case of N_3—PCL, significant weight loss started at 270°C, and finally all PCL burned out at 500°C (dotted line). As all of the grafted polymers are assumed to be lost at 500°C, the weight fraction of the PCL macromolecules in PCL-*g*-GF was determined to be 75% (solid line).

The morphology of the resulting PCL-*g*-GF was investigated by TEM observation. Figure 8(a) shows TEM image and selected area electron diffraction (SAED) pattern of pristine unmodified GF. The average lateral sizes of the multilayer GF were found to be 1 μm. The SAED exhibited a single set of hexagonal

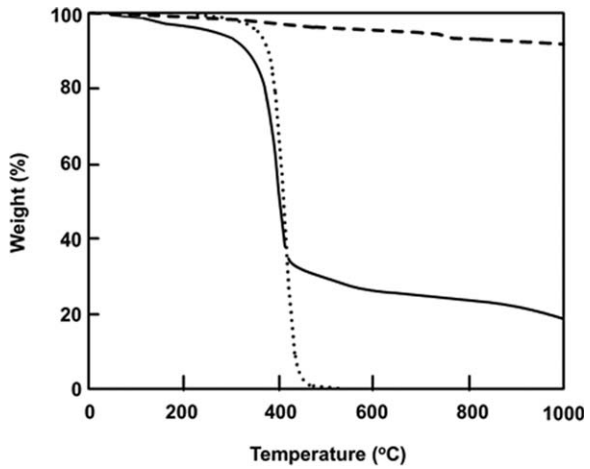


Figure 7. TGA curves of GF (dashed line), N_3—PCL (dotted line), and PCL-*g*-GF (solid line).

diffraction pattern with sharp and clear diffraction spots, indicating the high crystallinity of the graphene sheets. Figure 8(b) shows representative example of PCL-*g*-GF. The dark regions are related to the grafted PCL chains onto the surface of GF. It was worth mentioning that the morphology of PCL-*g*-GF did not change significantly after modification, indicating that PCL chains were successfully introduced on GF surface without disrupting the structure of GF.

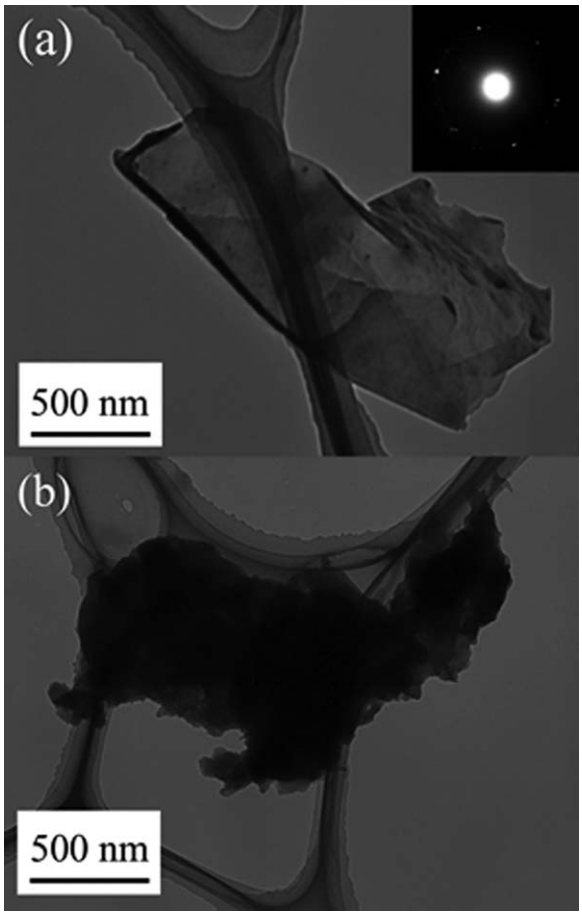


Figure 8. TEM images of (a) GF and (b) representative example of PCL-*g*-GF.

Table I. Dispersibility of PCL-*g*-GF and Solubility of N_3—PCL in Various Solvents

Solvent	Dispersibility of PCL-*g*-GF	Solubility of N_3—PCL
Hexane	Poor	Poor
Benzene	Good	Good
CH_2Cl_2	Good	Good
THF	Good	Good
NMP	Good	Good
CH_3OH	Poor	Poor

Table I summarizes dispersibility of PCL-*g*-GF in various organic solvents. A small amount (ca. 1 mg) of PCL-*g*-GF was added to 2 mL of solvents. Excellent dispersion was observed for dichloromethane, THF, benzene, and NMP. Conversely, sedimentation of black powder at the bottom was observed for methanol and hexane. For reference, solubility of N_3—PCL is also summarized in Table I. The dispersibility of PCL-*g*-GF was reasonably explained by the solubility of the attached PCL. It is safe to conclude that at least 75 wt % grafting of PCL macromolecules onto GF was enough to provide good dispersibility for GF. In fact, quantitative characterization of nanocarbon-based dispersion is important for the solution-based fabrication process. Liu et al. developed a simple and highly reproducible method for the quantitative analysis of carbon nanotube dispersions using dynamic light scattering techniques.[33,34] Our future work involves examination of solvent effect on dispersibility.

CONCLUSION

We have demonstrated functionalization of multilayer GF with a presynthesized well-defined PCL macromolecule to obtain PCL-*g*-GF which has high dispersibility in various organic solvents. The method for preparing PCL-*g*-GF is one-step nitrene chemistry using azido-terminated PCL. GPC, ^{1}H NMR, IR, Raman analysis indicated that PCL chains were introduced onto the surface of GF through covalent bond formation. UV-vis measurements revealed the successful grafting-on reaction without disrupting the electronic structure of GF. Incorporation of 75 wt % of PCL macromolecules on GF was enough to improve the dispersibility in a wide variety of organic solvents. Soluble GF composite is expected to find use for solution-based fabrication procedures.

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