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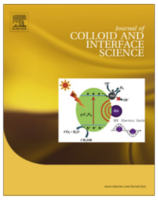

Regular Article

High-concentration graphene dispersion stabilized by block copolymers in ethanol

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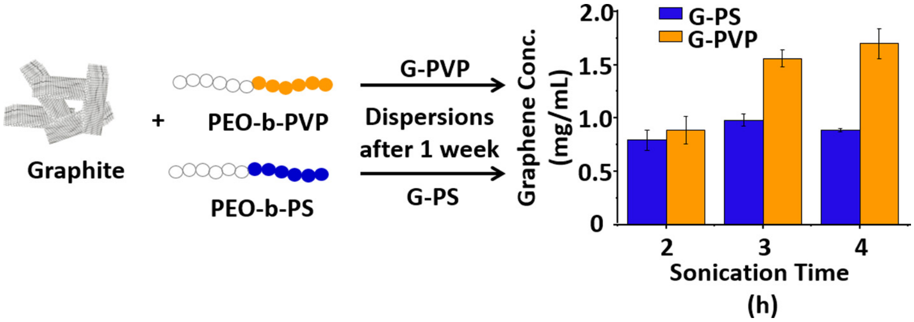
GRAPHICAL ABSTRACT



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ABSTRACT

This article describes a comprehensive study for the preparation of graphene dispersions by liquid-phase exfoliation using amphiphilic diblock copolymers; poly(ethylene oxide)-*block*-poly(styrene) (PEO-*b*-PS), poly(ethylene oxide)-*block*-poly(4-vinylpyridine) (PEO-*b*-PVP), and poly(ethylene oxide)-*block*-poly(pyrenemethyl methacrylate) (PEO-*b*-PPy) with similar block lengths. Block copolymers were prepared from PEO using the Steglich coupling reaction followed by reversible addition-fragmentation chain transfer (RAFT) polymerization. Graphite platelets (G) and reduced graphene oxide (rGO) were used as graphene sources. The dispersion stability of graphene in ethanol was comparatively investigated by on-line turbidity, and the graphene concentration in the dispersions was determined gravimetrically. Our results revealed that the graphene dispersions with PEO-*b*-PVP were much more stable and included graphene with fewer defects than that with PEO-*b*-PS or PEO-*b*-PPy, as confirmed by turbidity and Raman analyses. Gravimetry confirmed that graphene concentrations up to 1.7 and 1.8 mg/mL could be obtained from G and rGO dispersions, respectively, using PEO-*b*-PVP after one week. Distinctions in adhesion forces of PS, VP, PPy block units with graphene surface and the variation in solubility of the block copolymers in ethanol medium significantly affected the stability of the graphene dispersion.

1. Introduction

Graphene has attracted intense interest in recent years because of its unique properties [1]. Graphene has a mechanical strength of ~130 GPa, which is 200 times greater than that of steel, and it is 10 times more electrically conductive than copper [2,3]. The absorbance of white light by mechanically exfoliated single layer gra-

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phene is ~2.3% [4]. Dozens of methods have been developed and used to prepare graphene of various qualities. However, the mass production of graphene with specific properties for specific applications is still challenging. Graphenes are prepared by various methods, such as mechanical exfoliation, chemical vapor deposition (CVD) [5], silicon carbide (SiC) epitaxial growth [6], molecular assembly, and liquid-phase exfoliation [7,8]. These methods show promise for several applications, such as prototyping, coating, electronics [9], photonics [4], transistors [10], composites [8], inks, and energy storage [11]. However, some of the methods have several disadvantages. For example, SiC wafers are very expensive, and the removal of metal foil from CVD graphene is generally difficult for mass production. Among these methods, liquid-phase exfoliation has attracted much attention because mass production of graphene can be achieved at low cost, although the quality of graphene might be reduced [12]. In liquid-phase exfoliation, graphite splits into thinner platelets and prolonged treatment times yield single graphene platelets that become smaller in lateral size. Graphite was exfoliated with the aid of sonication in the presence of *N*-methyl-2-pyrrolidone (NMP), and a graphene concentration of up to 1.2 mg/mL could be attained after a long sonication period (~460 h) [13,14]. However, NMP is expensive and has a high boiling temperature, which renders it difficult to use in further processes. The use of low boiling solvents (e.g., alcohols) is highly desirable, but such solvents are not useful for the exfoliation of graphite due to unmatched surface energy. For this reason, surfactant-assisted liquid-phase exfoliation has been extensively explored [12,15]; however, this method also suffers from drawbacks such as desorption or migration of surfactant molecules, low attainable graphene concentration (0.3–0.9 mg/mL), extensive sonication, and re-aggregation of graphite platelets. Recently, various random or block copolymers showed promising results for graphene dispersion as stabilizers overcoming the drawbacks of short chain surfactants [7,8,16], but they were mostly limited to commercialized copolymers. In order to prepare highly stable graphene dispersions, it is essential to understand the affinity between the basal graphene and monomeric units comprising block copolymers.

Very recently, we reported the adhesion forces between several vinyl monomers and different graphene surfaces measured from the force-distance (F-d) curve analyses of atomic force microscopy (AFM) [17]. Based on the knowledge of the attractive interactions between the monomers and graphenes, we successfully designed and synthesized amphiphilic block copolymers and used for the stabilization of graphene nanoplatelets in alcohol and water [18,19]. The PVP block in PEO-*b*-PVP was varied to check the dispersibility of graphene in ethanol and water, and the graphene dispersibility could be enhanced accordingly with the length of PVP [18]. As a continuation of the previous work, three different amphiphilic block copolymers (PEO-*b*-PS, PEO-*b*-PVP, and PEO-*b*-PPy) with similar PEO block length using different graphene-philic blocks were synthesized and used as dispersants for graphite platelets (G) and reduced graphene oxide (rGO) in ethanol as a medium. The optimum dispersion conditions and destabilization behavior of the graphene dispersions were investigated and presented systematically based on the on-line turbidity, gravimetry, Raman, and electron microscopic analyses.

2. Materials and methods

2.1. Materials

Styrene (S, Junsei, Tokyo, Japan) and 4-vinylpyridine (VP, Sigma–Aldrich, MA, USA) were passed through an inhibitor remover column to remove hydroquinone. 1-Pyrenemethyl methacrylate (Py), Monomethoxy poly(ethylene glycol) (mPEO, M_n = 10,000 g/mol), 2,2′-azobisisobutyronitrile (AIBN), *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), dodecanethiol, tricaprylylmethylammonium chloride, carbon disulfide, 2-propanol, anhydrous potassium carbonate, anhydrous tetrahydrofuran (THF), anhydrous 1,4-dioxane, and anhydrous methylene chloride (DCM) were purchased from Sigma–Aldrich (MA, USA) and used as received. 2-(Dodecylthiocarbonothioyl thio)-2-methylpropionic acid (TTC) was synthesized according to literature procedure [20] and used as a RAFT agent. Graphite platelets (G, M-25, XG Sciences, USA) were donated from Research Institute of Industrial Science and Technology (RIST, Pohang, Korea). Reduced graphene oxide (rGO, rGO-V20-100, 4–8% oxygen) was also donated from Standard Graphene (Korea). All other solvents used for the experiments were purchased from Duksan Pure Chemicals Co., Ltd. (Seoul, Korea) and used as received.

2.2. Synthesis of the PEO macro-RAFT agent

The PEO macro-RAFT agent (PEO-TTC) was prepared by Steglich coupling, as shown in Scheme 1. Moisture was removed from mPEO by azeotropic distillation with toluene. To the mPEO (1.0 mmol) in DCM, TTC (3.0 mmol), DCC (3.0 mmol), and DMAP (0.3 mmol) were added and stirred for 24 h at room temperature. After the reaction, the mixture was filtered to remove the precipitates. Crude PEO-TTC was then precipitated in excess hexane three times to remove excess TTC. The structure of PEO-TTC was analyzed by proton nuclear magnetic resonance (^{1}H NMR) (Fig. S1), carbon nuclear magnetic resonance (^{13}C NMR) (Fig. S2), and size-exclusion chromatography (SEC) analyses (Figs. S6 and S7).

2.3. Synthesis of amphiphilic block copolymers

PEO-TTC (1.0 mmol), VP or S or Py (70.0 mmol), and AIBN (0.5 mmol) were dissolved in dioxane (5 mL), and three freeze-pumpthaw cycles were performed. Then the mixture was sealed after purging with N_2, immersed into a pre-heated oil bath at 70 °C, and stirred for 24 h (Scheme 2). The resulting block copolymers were precipitated in excess hexane for three times to remove the unreacted monomers (VP, S, or Py). Unreacted PEO-TTC was removed by washing with pure water three times, and which resulted in block copolymers. The block copolymers were characterized by ^{1}H NMR (Figs. S3–S5) in $CDCl_3$ and SEC in *N*,*N*-dimethylformamide (DMF) (Fig. S6, Table 1) or $CHCl_3$ (Fig. S7, Table 1).

2.4. Preparation of graphene dispersions using block copolymers and on-line turbidity measurements

For the preparation of the ethanolic graphene dispersion, 5 mg of each block copolymers and 10 mg of G or rGO in 4 mL of ethanol were sonicated for 2 h, 3 h, and 4 h in a bath sonicator (40 kHz, SH-2140, 190 W, Saehan, Korea). The initial G or rGO concentration was fixed as 2.5 mg/mL, and 50 wt% of the block copolymer (with respect to the weight of G or rGO) was used for all dispersion samples. After the desired sonication time, time-evolution backscattering data were measured by on-line turbidity (Turbiscan LAB, Formulaction Co., L'Union, France). From the backscattering data, the Turbiscan Stability Index (*TSI*) in the predefined zone (middle or top) of the vial bottle versus ageing time was obtained using the following equation:

$$TSI = \sum_i \frac{\sum_h |scan_i(h) - scan_{i-1}(h)|}{H} \qquad (1)$$