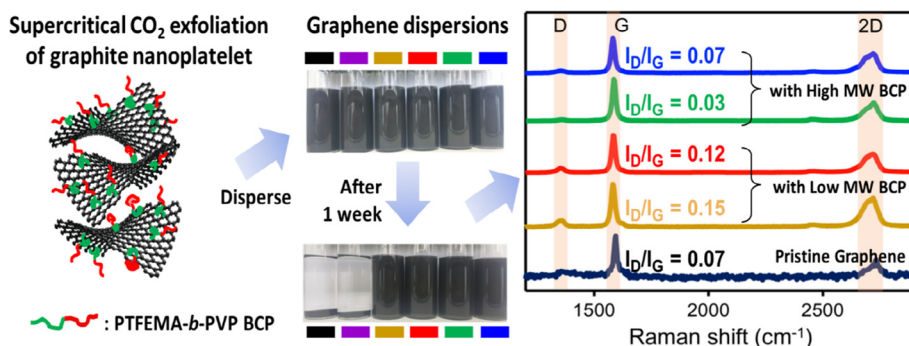




Regular Article

A study on amphiphilic fluorinated block copolymer in graphite exfoliation using supercritical CO₂ for stable graphene dispersionYoung Hyun Kim^a, Hyang Moo Lee^a, Sung Wook Choi^{b,*}, In Woo Cheong^{a,*}^a Department of Applied Chemistry, Kyungpook National University, Daehak-ro 80, Buk-gu, Daegu 41566, Republic of Korea^b Department of Biotechnology, The Catholic University of Korea, Bucheon-si, Gyeonggi-do, Republic of Korea

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, poly(2,2,2-trifluoroethyl methacrylate)-*block*-poly(4-vinylpyridine) (PTFEMA-*b*-PVP) was synthesized by stepwise reversible addition-fragmentation chain transfer (RAFT) polymerization for the preparation of graphene by the exfoliation of graphite nanoplatelets (GPs) in supercritical CO₂ (SCCO₂). Two different block copolymers (low and high molecular weights) were prepared with the same block ratio and used at different concentrations in the SCCO₂ process. The amount of PTFEMA-*b*-PVP adsorbed on the GPs and the electrical conductivity of the SCCO₂-treated GP samples were evaluated using thermogravimetric analysis (TGA) and four-point probe method, respectively. All GP samples treated with SCCO₂ were then dispersed in methanol and the dispersion stability was investigated using online turbidity measurements. The concentration and morphology of few-layer graphene stabilized with PTFEMA-*b*-PVP in the supernatant solution were investigated by gravimetry, scanning electron microscopy, and Raman spectroscopy. Destabilization study of the graphene dispersions revealed that the longer block copolymer exhibited better affinity for graphene, resulting in a higher yield of stable graphene with minimal defects.

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1. Introduction

Graphene, which has a 0.34 nm-thick, two-dimensional (2D), and *sp*²-bonded hexagonal structure, has been widely investigated owing to its unique and remarkable properties, such as its high Young's modulus, electron mobility, thermal conductivity, and

light transparency [1]. These unique properties have led to graphene being applied in composites [2], barrier coatings [3], solar cells [4], transistors [5], and biomedical applications [6].

However, the mass production of graphene at a reasonable cost remains a challenge. Bottom-up methods using small carbon sources, such as chemical vapor deposition and SiC epitaxial growth, incur high production costs and are not suitable for mass production [7,8]. Instead, mechanical or chemical exfoliation of graphite (e.g., liquid-phase exfoliation) may be applied to mass production. Although liquid-phase exfoliation is considered the most cost efficient method for graphene production, it suffers from aggregation and sedimentation [9]. To overcome these problems, many researchers have studied the covalent functionalization of graphite, which involves chemical oxidation using strong acids [10–12]. This chemical approach is a promising candidate for the production of few-layer graphene dispersions, but frequently results in defects that cause deterioration of its unique properties [13]. Non-covalent approaches involving ultrasonic [14] or microwave [15] treatment usually result in fewer defects but still require suitable stabilization strategies to maximize colloidal stability.

Recently, supercritical fluids like N,N-dimethylformamide (DMF) [16], ethanol [17], and CO₂ [18] have been used to intercalate or delaminate layered 2D-materials, such as MoS₂, BN, and graphite. In particular, supercritical CO₂ (SCCO₂) has been extensively studied owing to its mild supercritical conditions (T_c = 304.2 K, P_c = 7.4 MPa), non-toxicity, stability, recyclability, and high permeability [18,19]. SCCO₂ can facilitate the intercalation and exfoliation of graphite more efficiently with minimal defects. In addition, it enables facile recovery of CO₂ by simple depressurization. However, the exfoliation of graphite into few-layer graphene and the prevention of re-aggregation of graphene sheets under SCCO₂ remain challenging [20–22].

In this work, graphite nanoplatelet (GP) was exfoliated in SCCO₂ with poly(2,2,2-trifluoroethyl methacrylate)-*block*-poly(4-vinylpyridine) (PTFEMA-*b*-PVP) diblock copolymer and the resulting GP dispersions were prepared in methanol. Since the PVP block or PVP homopolymer is insoluble in SCCO₂, amphiphilic PTFEMA-*b*-PVP block copolymer was used instead of commercialized PVP homopolymer. PVP was chosen as a graphene-philic block because PVP shows high affinity to graphene, as confirmed by the force-distance analyses of AFM [25–28], while PTFEMA was used as a lyophilic block due to its high SCCO₂-solubility [23–29]. The effects of block length and amount of block copolymer used in the SCCO₂ treatment on the dispersion stability and electrical conductivities of graphite nanoplatelets were studied. After separation of relatively stable graphenes from the supernatant solutions, the hydrodynamic size, graphene concentration, and morphology of the few-layer graphene were also investigated.

2. Experimental

2.1. Materials

Both 2,2,2-Trifluoroethyl methacrylate (TFEMA, Fluorochem, UK) and 4-vinylpyridine (VP, 95%, Alfa Aesar, UK) were employed after purification using an inhibitor-removal column (inhibitor removers, Aldrich, USA). The compounds 4-Cyano-4-(phenylcarbo nothiylthio)pentanoic acid (CTP, 97%, Aldrich, USA), 1,4-dioxane (99.5%, Acros, USA), hexanes (95%, Duksan, Korea), tetrahydrofuran (THF, 99.5%, Duksan, Korea), and methanol (99.8%, Duksan, Korea) were used as received without further purification. 2,2'-Azobisisobutyronitrile (AIBN, 98%, Junsei, Japan) was used after recrystallization in methanol. Graphite nanoplatelets (GPs, M-25 grade, XG Sciences, USA) were used as the graphite source.

2.2. Preparation of block copolymers

As previously reported [26], PTFEMA-*b*-PVP block copolymers showed better graphene dispersion stability and higher graphene concentrations when each blocks are of similar length. Therefore, we prepared two different (low and high molecular weights) block copolymers while maintaining the same ratio of the PTFEMA and PVP blocks. The synthesis schemes for the PTFEMA-RAFT agents and PTFEMA-*b*-PVP block copolymers are shown in Scheme 1, and the molecular weights of the block copolymers are listed in Table 1. The two different block copolymers were characterized by proton nuclear magnetic resonance (¹H NMR) and size exclusion chromatography (SEC).

2.3. SCCO₂ treatment of GPs with block copolymers

The SCCO₂ treatment was performed in a custom-built autoclave reactor system. A flowchart for the SCCO₂ treatment of GPs with the block copolymers is shown in Scheme 2. First, the reactor vessel was charged with predetermined amounts of GPs and PTFEMA-*b*-PVP (amounts listed in Table 2). Liquefied CO₂ was then pumped from the CO₂ reservoir into the reactor vessel using a CO₂ injection pump where it was cooled to –20 °C with a chiller. The temperature and pressure of the vessel were increased to 55 °C and 100 bar, respectively. The mixture of GPs and block copolymer in SCCO₂ was stirred at 1000 rpm for 1 h. The vent valve was opened to allow rapid depressurization and obtain the SCCO₂-treated GP samples.

2.4. Preparation of SCCO₂-treated GP dispersions

The desired amount of SCCO₂-treated GP was collected from the entire samples to prepare GP dispersions (GPDs) in 20 mL of methanol. The compositions of GPDs are listed in Table 3. All dispersions were sonicated in a bath-type sonicator (SD 80 H, 40 kHz, 50 W, S-D Ultra Sonic Cleaner, Korea). To minimize the defect formation on graphene and size reduction during the 2 h sonication, a low-power ultrasonic bath was used and the temperature was maintained with a thermostat [36,37]. For comparison of dispersion stability, pristine GPs and GPs treated in SCCO₂ without block copolymer (designated as SCGP) were also used to prepare dispersions, designated as GPD and SCGPD, respectively.

2.5. Characterization

The molecular weights of PTFEMA-RAFT agents were measured by SEC (Alliance e2695, Waters, Empower Pro[®], USA). The SEC analysis was performed with a refractive index (RI) detector and three different columns (Styragel HR3, Styragel HR4, and Styragel HR5E; Waters, USA) in series. THF (>99.9%, Merck, Germany) was used as the eluent (35 °C, 1 mL/min). Polystyrene narrow standards (1060 and 3,580,000 g/mol, Waters, USA; 1320–2,580,000 g/mol, Shodex, Japan) were used for calibration. The chemical structures and molecular weights of the PTFEMA-RAFT reagents and PTFEMA-*b*-PVP block copolymers, respectively, were confirmed by ¹H NMR spectroscopy (AVANCE III, 500 MHz, Bruker, Germany) in chloroform-*d* containing 0.05% tetramethylsilane (Aldrich, USA).

To determine the amount of PTFEMA-*b*-PVP adsorbed on the GPs in SCCO₂ treatment, TGA (Q600, TA Instruments, USA) was performed. The electrical conductivity of the SCCO₂-treated GPs was measured using a four-point probe (RT-70, Napson, Korea). All samples were pelletized into coin shapes with 1.2 cm diameter with thicknesses ranging from 0.228 to 0.390 mm before measurement. To analyze the oxygen content of the graphite nanoplatelets before dispersion, X-ray photoelectron spectroscopy (XPS) was performed on a Quantera SXM ULVAC-PHI spectrometer (Physical

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