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Introduction

Polymer particles have been used in ubiquitous applications such as coatings, adhesives, and films in industrial fields over several decades.^{1,2} Recently, the application of polymer particles has expanded to intelligent materials in sophisticated industry fields, where polymer particles are used as for example drug transport carriers³⁻⁵ (e.g. drug delivery systems) and display materials in electronic paper.^{6,7} In order to enable such applications of polymer in the particle state, novel synthetic routes to polymer particles with multifunctional properties are required.

Graphene is an allotrope of carbon consisting of an atomically thin two-dimensional "nanosheet" structure.⁸⁻¹⁰ In 2004, Novoselov and Geim first reported the preparation and properties of graphene, in which graphene was prepared by mechanical exfoliation of graphite.8 Thereafter, many researchers have reported new synthetic methods and further properties of graphene.¹¹⁻¹⁵ As graphene possesses various functionalities such as impressive electrical, optical, thermal, and mechanical properties,¹⁶⁻¹⁸

Synthesis of polymeric nanoparticles containing reduced graphene oxide nanosheets stabilized by poly(ionic liquid) using miniemulsion polymerization

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Polymeric nanoparticles containing reduced graphene oxide (rGO) nanosheets have been prepared by aqueous miniemulsion radical polymerization of methyl methacrylate (MMA) utilizing poly(ionic liquid) (PIL) as stabilizer to effectively disperse the rGO nanosheets in the monomer phase. The PIL that gave the best results in terms of rGO dispersibility was a block copolymer of the ionic liquid monomer 1-(2methacryloyloxyethyl)-3-butylimidazolium bis(trifluoromethanesulfonyl)amide ([Mbim][TFSA]) and MMA, the concept being that the MMA units impart solubility in the MMA monomer droplets whereas the IL units act as adsorption sites for rGO. The rGO dispersibility in vinyl monomer was demonstrated to be superior using the above PIL block copolymer compared to the corresponding statistical copolymer or PIL homopolymer. Overall, the approach developed demonstrates how PILs can be employed to conveniently switch (turn ON/OFF) the dispersibility of PIL/rGO via anion exchange reactions, which can be an efficient strategy for synthesis of polymer/rGO nanocomposite materials.

> it has attracted much attention as a functional material in various fields. However, when graphene is used as filler in polymeric materials to enhance their properties, it is difficult to disperse within both a solid matrix or in a solvent due to strong van der Waals interactions between graphene layers, resulting in sheet aggregation. In order to improve the dispersibility of graphene, chemical modification of graphene and the use of surfactants have been reported.19-23

> Ionic liquids are composed of an organic cation and an organic or halogen anion and exist in the liquid state at room temperature.²⁴⁻²⁶ They have attracted attention due to their use as environmentally friendly media in various synthetic fields, as well as functional materials such as electrolytes²⁷⁻²⁹ and CO₂ separation membranes.^{30–32} Recently, imidazolium-based ionic liquids and poly(ionic liquid)s (PIL) prepared by the polymerization of ionic liquid monomer have received attention as a potential dispersant of graphene due to π - π interactions between imidazolium rings and graphene sheets.^{33–35} Graphene dispersions could be obtained in various solvents using PIL as dispersant because of the possibility to conveniently control the solubility of PIL by anion exchange, as reported by Suh and coworkers.35 In this particular case, graphene sheets modified by PIL were able to be transferred between the water phase and the oil phase by anion exchange.

> Miniemulsion polymerization is a useful method for preparation of hybrid nanoparticles composed of organic and inorganic materials, as well as hollow particles and various other

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Paper

structures³⁶⁻³⁹ including implementation of controlled/living radical polymerization.⁴⁰ Several groups have reported composite polymer particles containing graphene oxide (GO), which is the oxidized form of exfoliated sheets from graphite or graphene, prepared by miniemulsion polymerization.⁴¹⁻⁴⁵ We have successfully prepared composite nanoparticles "armoured" with GO nanosheets via miniemulsion polymerization, in which GO was used as the sole surfactant.^{46–52} Such polymer nanocomposite materials containing GO can be a precursor to composite materials containing reduced graphene oxide (rGO), as the functionality of rGO is similar to that of graphene. However, when reduction of GO to yield rGO is performed in the nanocomposite particle state, it is expected that colloidal stability will be compromised due to the loss of polar functional groups within the structure of GO (mainly carboxylic acid groups at the periphery of the sheets). In previous work, we demonstrated the preparation of PIL particles containing rGO by miniemulsion polymerization using rGO dispersed in an ionic liquid monomer.⁵³ However, with regards to industrial applications, there is a desire to develop methods applicable to conventional monomers such as styrenic and methacrylate monomers. In the present work, the preparation of rGO dispersions stabilized by poly(ionic liquid) in a conventional vinyl monomer was investigated. Thereafter, miniemulsion polymerization of the monomer dispersion was performed to yield composite nanoparticles.

Experimental

Materials

Methyl methacrylate (MMA, 99%, Aldrich) and ethyl methacrylate (EMA, 99%, Aldrich) were purified by passing through a column of activated basic aluminium oxide (Ajax) to remove the inhibitor. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich) was purified by recrystallization in methanol. 1-(2-Methacryloyloxyethyl)imidazole (MEIZ) (>95%, The Nippon Synthetic Chemical Industry Co., Ltd, Japan), hydrazine hydrate (Sigma Aldrich), 2-cyano-2-propyl benzodithioate (CPBD) (97%, Sigma Aldrich), ammonia solution (28 wt%), graphite nanofibers (Catalytic Materials Ltd, >98%), HCl (Ajax, 32 wt%), H₂SO₄ (Ajax, 98%), H₃PO₄ (BDH Chemical, 85%), KMnO₄ (Ajax), H₂O₂ (Ajax, 30 wt%), *n*-butylbromide, 1-ethylbromide, 1-vinylimidazole, (Nakalai Tesque Inc., Kyoto, Japan), lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) (99.7%, Kanto Chemical Co., Inc., Japan) were used as received. Deionized water was used in all experiments.

Preparation of ionic liquid monomer (1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide: [Veim][TFSA], 403.32 g mol⁻¹)

A typical synthesis of imidazolium-based hydrophobic ionic liquid monomers was carried out as reported in previous papers.⁵⁴ Firstly, [Veim]Br was prepared from 1-vinylimidazole

and 1-ethylbromide. 1-Ethylbromide (0.15 mol) was added dropwise into 1-vinylimidazole (0.13 mol) under vigorous stirring in methanol (10 g). The mixture was poured into a Schlenk flask, degassed using several vacuum/N₂ cycles, and then allowed to react in a heated water bath at 40 °C overnight with constant magnetic stirring (220 rpm). When the obtained solution was added dropwise into diethyl ether (300 mL), a white solid material was obtained, which was dried under vacuum and confirmed the structure by ¹H NMR. After the obtained [Veim]Br (0.11 mol, 20.5 g) was dissolved in water (25 mL), an aqueous solution (25 mL) of Li[TFSA] (0.12 mol, 28.7 g) was added to the [Veim]Br aqueous solution under vigorous stirring. After phase separation took place, the lower oily layer was collected, washed five times with distilled water and then dried under vacuum. [Veim][TFSA] was obtained as a pale yellow-colored liquid (yield: 93.0%) (Scheme 1).

Preparation of ionic liquid monomer (1-(2-methacryloyloxyethyl)-3butylimidazolium bis(trifluoromethanesulfonyl)amide: [Mbim][TFSA], 517.46 g mol⁻¹)

First, synthesis of [Mbim][TFSA] was carried out using MEIZ and *n*-butylbromide. MEIZ (5.0 g, 27.7 mmol) and *n*-butylbromide (4.0 g, 29.2 mmol) were mixed in methanol (10 g), the mixture was poured into a Schlenk flask, degassed using several vacuum/N₂ cycles, and then allowed to react in a water bath at 60 °C for 24 h with constant magnetic stirring (220 rpm). After purification of the obtained solution into diethyl ether (300 mL), a low viscosity yellow liquid was obtained, which was dried under vacuum. The structure was confirmed by ¹H NMR (yield: 65%). Anion exchange process to obtain [Mbim][TFSA] was carried out in water using [Mbim]Br (5.7 g, 18 mmol) and Li[TFSA] (4.8 g, 20 mmol) under the same conditions. [Mbim][TFSA] was obtained as a pale yellow liquid.

Preparation of GO from graphite nanofibers

GO was prepared by the oxidation of graphite nanofibers following a previous report.⁵⁰ Briefly, 2 g of graphite nanofibers was added to 250 mL of sulfuric acid and phosphoric acid (v/v = 9/1), followed by the slow addition of 12 g KMnO₄ to the mixture in an ice bath with stirring (the temperature was kept below 10 °C). The flask was placed in an oil bath at 45 °C for 17 h with magnetic stirring at 400 rpm to oxidize the graphite nanofibers. The mixture was poured onto ice (400 g), treated with 15 mL of 30 wt% H₂O₂ aqueous solution and then purified by centrifugation (8000 rpm, 8 min), followed by several washing cycles of 3.4 wt% HCl aqueous solution (3 times), acetone (3 times) and diethyl ether (2 times). The isolated material was dried in a vacuum oven (40 °C) and stored in a desiccator until use, and characterized by XPS and FT-IR spectroscopy.

[Veim][TFSA]

Scheme 1 Structure of ionic liquid monomers.



[Mbim][TFSA]

Preparation of poly([Veim][TFSA]) (PIL[TFSA]) and reduced graphene oxide (rGO) composite materials

A solution of PIL[TFSA] was prepared by solution polymerization in acetone. [Veim][TFSA] (5.0 g) and AIBN (0.5 g, 10 wt% based on monomer) were dissolved in acetone (10 g), transferred to a round-bottom Schlenk flask, sealed off with a silicon rubber septum, and purged with nitrogen for 5 min. Solution polymerization was carried out at 60 °C for 24 h with stirring.

PIL[TFSA]/rGO was prepared utilizing an anion exchange process and chemical reduction of as-prepared PIL[Br]/GO composite materials as outlined in a previous report.³⁵ GO powder (10 mg) was added to the PIL[TFSA]/acetone solution (0.11 g, 35 wt%). After ultrasonication for 10 min, a GO dispersion in PIL[TFSA]/ acetone solution was obtained. Subsequently LiBr (0.2 g) was added to this dispersion with stirring for 24 h at room temperature to obtain PIL[Br]/GO composite, resulting in a brown precipitate. The precipitate was washed with acetone (3 times), and then dried at room temperature under vacuum, and subsequently analyzed by XPS. The obtained PIL[Br]/GO powder (5 mg) was added to water (10 g), and ultrasonicated for 1 h to prepare a PIL[Br]/GO aqueous dispersion. The chemical reduction of PIL[Br]/GO occurred via the addition of 10 µL of hydrazine hydrate and 20 µL of ammonium solution (28 wt%), followed by heating and stirring at 95 °C for 30 min. The resulting dispersion was washed with water via centrifugation (10000 rpm, 20 min, 3 times), and dried at room temperature under vacuum, and then analyzed with XPS. In order to prepare PIL[TFSA]/rGO, Li[TFSA] (30 mg) was added to the PIL[Br]/rGO aqueous dispersion, and reacted for 24 h at room temperature. After washing with water (3 times) and drying in a vacuum oven (40 °C), a black material was obtained, which was analysed by XPS.

Preparation of poly([Veim][TFSA]-*stat*-MMA) statistical copolymer by solution polymerization

[Veim][TFSA] (5.0 g, 12.4 mmol), MMA (0.53 g, 5.3 mmol) and AIBN (0.55 g, 10 wt% based on monomer) were dissolved in acetone (10 g), transferred to a round-bottom Schlenk flask, sealed off with a silicon rubber septum, and purged with nitrogen for 5 min. Solution polymerization was carried out at 60 °C for 24 h. The product was precipitated in water/ethanol (w/w = 50/50, 300 mL) to remove the residual monomer and subsequently dried under vacuum at room temperature.

Preparation of poly([Mbim][TFSA]-*stat*-MMA) statistical copolymer by solution polymerization

This polymer was prepared using [Mbim][TFSA] (6.42 g, 5.3 mmol), MMA (0.53 g, 5.3 mmol) and AIBN (0.55 g, 10 wt% based on monomer) following the same procedure as above, except that precipitation was conducted in ethanol (300 mL).

Preparation of poly(MMA-*b*-[Mbim][TFSA]) block copolymer by solution reversible addition-fragmentation chain transfer (RAFT) polymerization

MMA (2.7 g, 28 mmol), CPBD (30 mg, 140 μ mol) as RAFT agent, and AIBN (9.0 mg, 55 μ mol) were dissolved in THF (6.0 g).

The reaction mixture was transferred to a round-bottom Schlenk flask, sealed off with a silicon rubber septum, and purged with nitrogen for 5 min. Solution RAFT polymerization was carried out at 60 °C for 18 h. The polymer was isolated by precipitation in hexane (300 mL) to yield PMMA (macroRAFT agent) as a pink powder. The monomer conversion was determined to be 74% via gas chromatography (GC-2014, Shimadzu Corp., Kyoto, Japan) with helium as the carrier gas, THF as the solvent, and *p*-xylene as the internal standard. The number-average molecular weight (M_n) and molecular weight distribution (MWD) were analyzed via gel permeation chromatography (GPC) at 40 °C using two styrene/divinylbenzene gel columns [Tosoh Corp., TSK gel GMH_{HR}-H, 7.8 mm i.d. \times 30 cm] with THF as the eluent, a flow rate of 1.0 mL min⁻¹, a refractive index (RI) detector (TOSOH RI-8020/21). The columns were calibrated with polystyrene calibration standards ($M_{\rm W}$ = 1.05 \times 10³-5.48 \times 10^6 g mol⁻¹, M_w/M_n = 1.01–1.15). The theoretical molecular weight $(M_{n,th})$ value was calculated using the following equation:

$$M_{n,th} = M_{RAFT agent} + \frac{[Monomer]}{[RAFT]} \times M_{monomer} \times Conversion$$

where $M_{\text{RAFT agent}}$ denotes the molecular weight of the RAFT agent or the macroRAFT agent. In this system, M_{n} and $M_{\text{w}}/M_{\text{n}}$ of the obtained PMMA are 17 000 g mol⁻¹ and 1.13, respectively $(M_{\text{n,th}} = 15\,000 \text{ g mol}^{-1})$.

The obtained PMMA macroRAFT agent (0.2 g, 12 µmol), [Mbim][TFSA] (0.5 g, 0.97 mmol) and AIBN (0.79 mg, 4.8 µmol) were dissolved in acetone (3.0 g). The solution was transferred to a round-bottom Schlenk flask, sealed off with a silicon rubber septum, and purged with nitrogen for 5 min. Solution polymerization was carried out at 60 °C for 18 h. The monomer conversion was determined to be 73% *via* ¹H NMR based on the vinyl H of the monomer (5.1 and 6.1 ppm). Moreover, the polymer was isolated by precipitation in ethanol (300 mL), and M_n of the obtained block copolymer was calculated as 35 516 g mol⁻¹ (poly(MMA₁₆₅-*b*-[Mbim][TFSA]₆₉)) based on ¹H NMR in acetone-*d*₆ by comparing peak integral of imidazolium part (9.0 ppm) in [Mbim][TFSA] to methoxy groups (3.7 ppm) in macroRAFT agent.

Miniemulsion polymerization with PIL copolymer and rGO

Poly([Veim][TFSA]-*stat*-MMA) (4.5 mg) and hexadecane (50 mg) were dissolved in EMA (1.0 g) at 60 $^{\circ}$ C, followed by addition of rGO (1.0 mg). After ultrasonication at 50% amplitude for 1 min, rGO dispersed in EMA was obtained. After addition of AIBN (40 mg), the dispersion was added to a 1 wt% Tween 80 aqueous solution (15 g), followed by ultrasonication for 5 min. The obtained emulsion was subsequently transferred to a round-bottom Schlenk flask, sealed with a silicon rubber septum, and purged with nitrogen for 5 min. Miniemulsion polymerization was carried out at 60 $^{\circ}$ C for 24 h at 240 rpm stirring.

In the case of using poly(MMA-*b*-[Mbim][TFSA]), the block copolymer (5.0 mg), hexadecane (40 mg) and AIBN (40 mg) were dissolved in MMA (1.0 g) at room temperature, followed by addition of rGO (1.0 mg). After ultrasonication at 50% amplitude for 20 min, rGO dispersed in MMA was obtained.

Miniemulsion polymerization was carried out under the same conditions as above.

Characterization

TEM images were obtained using a JEOL1400 transmission electron microscope at an accelerating voltage of 100 kV. The specimens were prepared by casting a drop of diluted aqueous polymerized miniemulsion onto a Formvar-coated copper grid followed by drying at room temperature. X-Ray photoelectron spectra (XPS) were recorded using a Kratos Axis ULTRA XPS using monochromatic Al X-rays (1486.6 eV) at 225 W (15 kV, 15 mA). Survey scans were carried out over 1360–0 eV binding energy range with 1 eV steps and a dwell time of 100 ms; high resolution scans were run with 0.2 eV steps and a dwell time of 250 ms. The chemical structures of ionic liquid monomer were confirmed by ¹H NMR. The ¹H NMR measurements were carried out with a Bruker Avance 500 MHz spectrometer at room temperature in D₂O.

Results and discussion

Preparation of PIL[TFSA]/rGO composite

In its pure form, rGO cannot be effectively dispersed in hydrophobic monomers. In order to increase the level of compatibility, rGO was modified with hydrophobic PIL. The hydrophobicity/ hydrophilicity of PIL can be tuned by changing the anion; PIL[TFSA] is hydrophobic whereas PIL[Br] is hydrophilic. The lateral dimensions of the GO sheets employed in this work were approximately 100 nm (DLS). GO was ultrasonicated in a PIL[TFSA] acetone solution according to a previous procedure,³⁵ yielding a stable brown dispersion (Fig. 1a). The reduction of GO with hydrazine is generally performed in water, which thus requires that PIL/GO can be dispersed in water. Anion exchange treatment of PIL[TFSA]/GO with LiBr resulted in formation of the more hydrophilic PIL[Br]/GO, which can be dispersed in water. As shown in Fig. 1, a brown material precipitated after addition of LiBr to the acetone dispersion. XPS analysis of the precipitate (Fig. 1, right), revealed two strong signals corresponding to N and Br, consistent with the formation of PIL[Br]/GO. The compositions calculated from XPS on the basis of Wang's report 55 were 20.4 wt% (GO) and 79.6 wt% (PIL[Br]), which is close to the initial stoichiometry.



Fig. 1 Visual appearances (left) of GO dispersion in PIL[TFSA] acetone solution before (a) and after (b) addition of LiBr. XPS wide scan spectra (right panel) of GO (a) and PIL[Br]/GO (b).



Fig. 2 Visual appearances (left) of PIL[Br]/GO dispersion in water before (a) and after (b) chemical reduction. XPS wide scan spectra (right panel) of PIL[Br]/GO before (a) and after (b) chemical reduction.

PIL[Br]/GO was readily dispersed in water, which enabled aqueous phase chemical reduction of GO to be performed using ammonium solution and hydrazine monohydrate at 90 °C. Fig. 2 shows the XPS spectra of PIL[Br]/GO before and after reduction. The color of the dispersion changed from dark brown to black, a visual cue that the chemical reduction of GO had proceeded.

Typically, the XPS peak corresponding to atomic oxygen should decrease when rGO is prepared from reduction of GO. However, N and Br signals (present in PIL[Br]) decreased instead of the O signal (present in GO), consistent with desorption of PIL[Br] from the GO surface (Fig. 2b). It is proposed that reduction of GO by hydrazine and ammonium aqueous solution proceeds simultaneously with anion exchange of PIL[Br]. Hydroxide (OH) ion and hydrogen carbonate (HCO₃) ion derived from CO₂ are present in the aqueous phase, and these ions may partake in anion exchange reaction with PIL[Br], thus replacing Br. Anion exchange of PIL[Br] would render the polymer more hydrophilic, thus making it more prone to dissolution in water relative to adsorption at the GO.

Due to the issues encountered with the above synthetic route, PIL[TFSA]/rGO was instead synthesized *via* an alternative process whereby rGO was first prepared *via* reduction of an aqueous GO dispersion,⁵³ followed by synthesis of PIL[TFSA]/rGO utilizing a two-step anion exchange process (Fig. 3). As the first step, rGO was dispersed in PIL[TFSA] acetone solution by ultrasonication for 10 min (Fig. 3a), demonstrating that PIL[TFSA] performed well as stabilizer of rGO (in the absence of PIL[TFSA], rGO agglomerated (coagulation) instantaneously in pure acetone after 10 min ultrasonication). PIL[TFSA]/rGO has



Fig. 3 Visual appearances (a–d) of synthesis process of PIL[TFSA]/rGO composite materials utilizing anion exchange: (a) PIL[TFSA]/rGO dispersion prepared by ultrasonication in acetone, (b) after addition of LiBr to PIL[TFSA]/rGO dispersion in acetone, (c) aqueous dispersion of PIL[Br]/rGO, and (d) after addition of Li[TFSA] to PIL[Br]/rGO aqueous dispersion.



Fig. 4 XPS wide scan spectra of rGO (a), PIL[Br]/rGO (b), and PIL[TFSA]/rGO (c).

now been prepared – however, in order to isolate this composite material as a solid, two anion exchange steps were performed. First, after addition of LiBr to the dispersion, phase separation occurred (Fig. 3b) due to the insolubility of the formed PIL[Br] in acetone. Interestingly, the precipitate obtained after washing with acetone could be dispersed instantaneously in water without ultrasonication (Fig. 3c). Subsequently, when Li[TFSA] was added to the aqueous dispersion, a black precipitate was obtained due to anion exchange from the bromide (hydrophilic) to [TFSA] (hydrophobic) anion (Fig. 3d). This precipitate (after washing with water) could be dispersed in acetone without ultrasonication, demonstrating how the dispersibility of PIL/ rGO can be readily switched utilizing anion exchange.

After the first anion exchange process (a) to (b) in Fig. 3, the atomic percentages of N and Br increased compared to the original rGO. These peaks correspond to PIL[Br], which accounts for 66 wt% of the total weight from calculation of the fractional composition based on the XPS data. After the second anion exchange process, the signal corresponding to Br disappeared, coupled with the appearance of a signal from F and S (present in the TFSA counterion). These results indicate that anion exchange proceeded efficiently and the obtained material was indeed PIL[TFSA]/rGO (Fig. 4).

Miniemulsion polymerization with PIL/rGO

Prior to miniemulsion polymerization, the dispersibility of PIL[TFSA]/rGO in various monomers was investigated. Although rGO precipitates instantaneously in common vinyl monomers, PIL[TFSA]/rGO is expected to be dispersible in some monomers similar to the acetone system described above. However, the dispersibility was poor in most monomers, although swelling was observed for MMA and EMA (Table 1).

To improve the solubility of PIL[TFSA] *i.e.* poly([Veim][TFSA]) in monomer, a statistical copolymer of [Veim][TFSA] and MMA was prepared, and its solubility in various monomers was subsequently examined. Poly([Veim][TFSA]-*stat*-MMA) (mol/mol = 70/30 assuming 100% monomer conversion) was soluble in EMA at 60 °C up to 0.45 wt%. rGO was subsequently dispersed in EMA/ copolymer (0.45 wt% copolymer in EMA) by ultrasonication, resulting in a dispersion that remained stable for approximately

 Table 1
 Dispersibility and solubility tests^a of PIL[TFSA]/rGO and PIL[TFSA], respectively, in various monomers

	PIL[TFSA]/rGO	PIL[TFSA]
Styrene	×	×
MMA	\bigtriangleup	\triangle
EMA	\bigtriangleup	\triangle
LMA	×	×
BzMA	×	×
PhEMA	×	×
t-BA	×	×
^{<i>a</i>} \times : not dispersil	ble or insoluble, \triangle : swelling.	

10 min (Fig. 5a). The rGO remained dispersed in EMA when the dispersion was added to Tween 80 aqueous solution (Fig. 5b), with no observable rGO precipitate from the deep blue miniemulsion that was obtained after ultrasonication (Fig. 5c). After miniemulsion polymerization using AIBN at 60 °C for 24 h, the color of the miniemulsion remained grayish but significant rGO precipitation was observed (Fig. 5d). As shown in Fig. 5e and f, the diameter of the obtained particles was approximately 50 nm. TEM imaging revealed enhanced contrast around the perimeter of the particles, possibly indicating some rGO had precipitated from inside particles (Fig. 5e). For comparison, a control experiment was conducted without copolymer, in which case rGO instantaneously precipitated in EMA, and the contrast around the perimeter of the obtained particles after polymerization was even more clearly observed (Fig. 5g). These results indicated that



Fig. 5 Visual appearances of the synthesis process of polymer particles containing rGO by miniemulsion polymerization: (a) rGO dispersion in EMA/copolymer; (b) rGO dispersed monomer in Tween 80 aq. before and (c) after ultrasonication; (d) obtained emulsion after miniemulsion polymerization; (e) TEM photograph of obtained particles; (f) number-based DLS distributions of diameter of obtained particles prepared by miniemulsion polymerization of rGO-dispersed EMA; (g) TEM photograph of obtained particles by miniemulsion polymerization of EMA/rGO droplets in Tween 80 aqueous solution.

some rGO is expected to be located inside the particles in the presence of poly([Veim][TFSA]-*stat*-MMA). Nevertheless, most rGO appeared to have precipitated and was located at the bottom of the emulsion, demonstrating that the rGO stability in monomer using this statistical copolymer was insufficient.

The concept of using poly[[Veim][TFSA]-*stat*-MMA) to enhance the stability of rGO in monomer is that the MMA units impart solubility in the monomer whereas the IL units act as adsorption sites for rGO. From this perspective, a statistical copolymer chain structure may have been far from optimal – a block copolymer with distinct IL and MMA segments would be expected to be more efficient.

Block copolymer synthesis with MMA/IL monomer was therefore conducted using RAFT polymerization with a methacrylate ionic liquid monomer ([Mbim][TFSA]; [Mbim][TFSA]:[MMA] = 70:30 mol/mol) instead of [Veim][TFSA] (because [Veim][TFSA] is an unconjugated monomer and thus difficult to polymerize using RAFT). First of all, in order to investigate whether the change in IL monomer type had any influence on the rGO stability, the statistical copolymer poly([Mbim][TFSA]-stat-MMA) was also prepared (same molar composition as poly[[Veim][TFSA]stat-MMA)). Poly([Mbim][TFSA]-stat-MMA) exhibited better solubility in monomer (soluble in MMA, and swollen by EMA) than poly([Veim][TFSA]-stat-MMA), but rGO/MMA in the presence of either copolymer remained stable for less than 10 min. The block copolymer PMMA-b-poly([Mbim][TFSA]) was soluble in EMA as well as MMA at room temperature, suggesting that the monomer solubility was remarkably improved by changing the structure from statistical copolymer to block copolymer. Moreover, a dispersion of rGO in MMA in the presence of the block copolymer (0.5 wt%; by ultrasonication) remained stable for at least 12 h (Fig. 6a), i.e. a significant improvement compared to the systems using either statistical copolymer, despite the same PIL content in the block copolymer (70 mol%) as that of the statistical copolymers (70 mol%). As shown in Fig. 6b, rGO dispersed in monomer remained stable after addition of the rGO dispersion to a 1 wt% Tween 80 aqueous solution. After ultrasonication, a milky-gray stable emulsion was obtained

with some minimal rGO precipitation at the bottom of the emulsion (Fig. 6c). When miniemulsion polymerization was carried out using AIBN at 60 °C for 24 h, the miniemulsion after polymerization was stable and the obtained particles were spherical based on TEM imaging (Fig. 6d and e). Quantitative analysis by gravimetry revealed that 30 wt% of the rGO had precipitated before polymerization, and the amount of precipitated rGO remained constant throughout the polymerization. When removal of rGO was performed by centrifugation (10000 rpm, 2 min) prior to miniemulsion polymerization, no rGO precipitate was observed after polymerization, resulting in successful formation of similarly sized polymeric nanoparticles (Fig. 6f and g). This result suggests that rGO precipitation mainly occurred during the ultrasonication step as opposed to during the actual polymerization, with 70 wt% of the initial rGO being located inside the obtained particles.

In order to confirm the existence of rGO inside the particles, the final emulsion was treated with acetone to dissolve PMMA following the same procedure previously reported.53 As shown in Fig. 7a, the solution after acetone treatment exhibited the Tyndall effect, unlike acetone solutions of PMMA and PMMA-bpoly([Mbim][TFSA]) in the absence of rGO. This would be due to dispersed rGO stabilized by π - π interactions between rGO and PIL units of block copolymer in acetone after dissolution of the PMMA particles. The particle size distribution (DLS; Fig. 7b) before acetone treatment comprised nanometer-sized particles $(D_n = 160 \text{ nm})$, consistent with the TEM imaging (Fig. 6g). After acetone treatment, significantly smaller nanoparticles ($D_n = 27 \text{ nm}$) were detected, consistent with single rGO sheets. The size reduction of rGO (compared to that of the initial GO) was due to further ultrasonication during the synthesis of rGO as well as during the preparation of rGO dispersed in monomer. Based on a particle diameter of 160 nm and assuming circular disc-like rGO sheets of diameter 27 nm and considering 70 wt% of the initially loaded rGO being located within the polymer particles,⁵³ one arrives at an average of 1.4 rGO sheets per particle, *i.e.* one rGO sheet in every particles. From these results, it has been demonstrated that PMMA composite particles containing rGO using PMMA-b-poly([Mbim][TFSA]) were successfully prepared.



Fig. 6 Synthetic route to polymer particles containing rGO by miniemulsion polymerization: (a) rGO dispersion in MMA/block copolymer, (b) rGO-dispersed MMA in Tween 80 aqueous solution before and (c) after ultrasonication; (d) emulsion obtained after miniemulsion polymerization; (e) TEM photograph of obtained particles; emulsion (f) and obtained particles (g) after polymerization of emulsion which was removed free rGO by centrifugation.



Fig. 7 (a) Observation of Tyndall phenomenon using a laser pointer for (left) emulsion after acetone treatment and (right) acetone solution dissolving PMMA and PMMA-*b*-poly([Mbim][TFSA]); and (b) number-based DLS distributions of diameter of PMMA particles containing rGO prepared by miniemulsion polymerization (line) and after acetone treatment (dashed line).

Conclusions

A novel approach towards synthesis of polymeric nanoparticles containing rGO nanosheets (lateral dimensions of approximately 27 nm) within the particle interior has been developed. The approach is based on aqueous miniemulsion radical polymerization using the nonionic surfactant Tween 80. The challenge of effectively dispersing the rGO nanosheets in the monomer phase (EMA or MMA) was overcome by use of poly(ionic liquid) (PIL) as stabilizer. The most effective stabilization was achieved using a block copolymer of the ionic liquid monomer [Mbim] [TFSA] and MMA, the concept being that the MMA units impart solubility in the MMA monomer droplets whereas the IL units act as adsorption sites for rGO. The rGO dispersibility in vinyl monomer was demonstrated to be far superior using the above PIL block copolymer compared to the corresponding statistical copolymer or PIL homopolymer. Overall, this work has demonstrated the preparation of composite polymeric nanoparticles containing rGO via the miniemulsion technique, with a view towards expanding the range of applicable monomers that can be used to prepare such nanocomposite materials.

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