Supporting Information

Electrically Conductive Polymer/rGO Nanocomposite Films at Ambient Temperature via Miniemulsion Polymerization Using GO as Surfactant

Yasemin Fadil¹, Vipul Agarwal¹, Florent Jasinski¹, Stuart C. Thickett², Hideto Minami³, Per

B. Zetterlund^{1*}

¹Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering,

University of New South Wales, Sydney, NSW 2052, Australia E-mail:

p.zetterlund@unsw.edu.au

² School of Natural Sciences (Chemistry), University of Tasmania, Hobart, TAS 7005, Australia
³ Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe
University, Rokko, Nada, Japan

Experimental

Materials

Styrene (St, Sigma Aldrich, 99%) and n-butyl acrylate (nBA, Sigma Aldrich, 99%) were purified by passing through a column of activated basic aluminium oxide (Ajax) to remove the inhibitor. Azobisisobutyronitrile (AIBN, Aldrich) was purified by recrystallization from acetone in water. Hexadecane (HD, 99%, Sigma Aldrich), sodium dodecyl sulfate (SDS, Ajax Finechem), and graphene oxide (GO; Graphenea) dispersed in water (4mg/1mL; average size 300 nm) were used as received. The water used in all experiments was MilliQ water.

Preparation of GO Nanosheets

The size of the GO sheets was reduced by ultrasonication (Branson Digital Sonifier 450) of an aqueous dispersion of GO (4 mg/ml) at 70% amplitude while on ice, resulting in a number-average size of ~30 nm as indicated by dynamic light scattering (DLS) - this GO is referred to as "small GO". The GO sheets as received are referred to as "large GO" This size measurement is a very approximate estimate at best, given that DLS theory is based on spherical objects.

Preparation of P(St-stat-nBA) GO Armoured Latex by Miniemulsion Polymerization

Miniemulsions were prepared using a mixture of styrene and n-butyl acrylate with the ratio of 50:50 wt% to target a film-forming system with an approximate theoretical glass transition temperature (T_g) of 3 °C (according to the Fox Equation).¹ 5 wt% and 2.5 wt% of GO (based on 1.05 g monomer) was dispersed in 15 ml of water and ultrasonicated for 10 min on ice (Branson Digital Sonifier at 70% amplitude). The organic phase consisting of AIBN (0.25 M rel. to organic phase), hexadecane (5 wt% rel. to total monomer) and monomer styrene (1.05 g) was prepared separately. The two phases and 0.25/0.5/1 wt% SDS rel. to organic phase were mixed and stirred using magnetic stirring for 30 min, then ultrasonicated for 10 min on ice (70% amplitude) to form the miniemulsion. The miniemulsion was degassed by nitrogen bubbling for 15 min. Polymerization was conducted in a sealed 25 mL glass bottle at 70 °C for 24 h under constant stirring. The precise amounts of GO, SDS, and AIBN used in each experiment are detailed in Table 1. **Table S1.** Recipes for AIBN-initiated miniemulsion polymerization of St/nBA (50:50 wt%) at 70 °C (amount of monomer fixed at 7 wt% relative to water and HD fixed at 5 wt% relative to monomer).

	LARGE GO		SMALL GO	
Experiment	GO	SDS	GO	SDS
	(wt%) ^ª	(wt%) ^b	(wt%) ^a	(wt%) ^b
A0	2.5	0	-	-
A1	2.5	0.25	-	-
A2	2.5	0.5	-	-
A3	2.5	1	-	-
B0	5	0	-	-
B1	5	0.25		
B2	5	0.5	-	-
B3	5	1	-	-
C0	-	-	2.5	0
C1	-	-	2.5	0.25
C2	-	-	2.5	0.5
C3	-	-	2.5	1
D0	-	-	5	0
D1			5	0.25
D2	-	-	5	0.5
D3	-	-	5	1

Preparation of P(St-stat-nBA)/GO Nanocomposite Film

Nanocomposite films were prepared by the drop casting method using 50 μ m of the polymer/GO latex onto a cleaned glass slide. The drop was allowed to dry under ambient conditions for 24 h.

Reduction of GO

P(St-*stat*-nBA)/GO nanocomposite films were heated in an oven at 160 ° C for 24 h, thus reducing GO to reduced graphene oxide (rGO).

Gravimetric analysis

Conversion of monomer into polymer was determined by gravimetry. The evolution of the monomer conversion over time was followed by taking latex samples at different time intervals. Approximately 1.5 g of latex was weighed into a pre-weighed aluminium pan and placed in a vacuum oven at 40 °C for 24 h.

rGO mass ratio in final film

The rGO mass ratio in the final film was estimated based on the initial miniemulsion polymerization stoichiometry in combination with gravimetry and thermogravimetric analysis (TGA). The initial mass ratio of GO is known from the recipe. The mass loss caused by GO being converted to rGO during thermal reduction was measured by TGA (Perkin Elmer STA 6000). Pure GO was heated to 160 °C at 10 °C/min, followed by an isothermal stage at this temperature for 24 h under air, resulting in a mass loss of 48%. The monomer conversion was subsequently determined via gravimetry, and thus the mass ratio of GO

4

(rGO) is readily calculated relative to the amount of polymer formed, taking into account the mass loss as GO was reduced to rGO (Table S8).

Gel Permeation Chromatography (GPC)

Number-average (M_n), weight-average (M_w) molecular weights and molecular weight distributions (MWDs) were determined by GPC. The GPC instrument was equipped with a DGU-12A solvent degasser, an LC-10AT pump, a CTO-10A column oven, a ECR 7515-A refractive index detector, and a Polymer Laboratories 5.0 µm bead-size guard column (50 × 7.8 mm) followed by four 300 × 7.8 mm linear Phenogel columns. The eluent was THF at 40 °C at a flow rate of 1.0 mL min⁻¹ with injection volume of 100 µL. The system was calibrated against linear poly(styrene) standards ranging from 500 to 10⁶ g mol⁻¹. Samples were prepared by dissolving 4 - 5 mg of dried polymer in 2 mL of THF, followed by filtration using a syringe filter (0.45 µm) to remove GO and impurities.

Dynamic Light Scattering (DLS)

The size of the GO sheets was estimated by DLS operating a 4 mW He-Ne laser at 633 nm at 25 °C at an angle of 173 °. The measurement was based on an average of five runs using a Malvern Zetasizer NanoSeries with DTS software. Samples to estimate the size of GO sheets were prepared by diluting a drop of aqueous GO dispersion (approx. 10⁻⁴ mg/ml) with MilliQ water. Size measurements of the polymer particles were conducted using the same instrument, by diluting a drop of latex (approx. 10⁻⁴ mg/mL) with MilliQ water based on an average of three runs.

Proton Nuclear Magnetic Resonance Spectroscopy (¹H NMR)

The chemical compositions of the copolymers were determined using ¹H NMR on a Bruker Av300 (300 MHz) spectrometer with auto-sampler at 25 ° C based on the equation below:

St % =
$$\frac{A/5}{A/5 + B/2}$$
 x 100 Equation S1

where St% is the mol% of styrene in the copolymer, A and B are the integrated areas of styrene (integrals of the phenyl protons at 6.7-7.1 ppm) and butyl acrylate (proton peak integrals of –OCH2 groups at 3.9 ppm) units.² The sample for P(St-*stat*-nBA)/GO was prepared by dissolving approximately 5 mg of the dried polymer in 1 mL deuterated chloroform (CDCl3).

Scanning Electron Microscopy (SEM)

SEM was used to investigate the surface morphology of the nanocomposite films. SEM images of film were recorded on a FEI Nova NanoSEM 230 at a working distance of approximately 5 mm and an accelerating voltage of 5 kV. The samples were carbon coated prior to imaging.

Differential Scanning Calorimetry (DSC)

DSC measurements to determine the glass transition temperatures of the films were performed on a TA DSC Q20 under nitrogen flux. The temperature ranged between -40 and 150 °C with a heating rate of 5 °C/min.

Contact Angle Measurements

Contact angles were determined using an optical tensiometer (Attension tensiometer, Biolin Scientific). A 2 μ L Milli-Q water droplet was placed onto the surface of the film, and the image of the drop was captured and analysed. Results were obtained based on average contact angle measurements for 2 individual films and 4 measurements per film.

Conductivity Measurements

The electrical conductivity of the nanocomposite films was determined using a standard four-point probe method (Jandel Model RM3). Results were obtained based on average conductivity results of two individual films and three measurements per film.

Optical Profilometry

The surface thickness of the nanocomposite films were determined using 3D non-contact optical profilometer (Bruker, ContourGT) with height 12 ± 1 nm. The reference was set as glass surface on either side of the film.

Optical Microscope

Microscope observations were conducted on a Leica optical microscope and all images were recorded using a IC80 HD digital camera.

Table S2. Conversion, intensity-average particle diameter (di) and pdi for miniemulsion
polymerization of St/nBA at 70 $^\circ$ C at different concentrations of SDS and GO (small and
large).

	LARGE GO SHEETS						SMALL GO SHEETS					
	2.5 wt% GO			5 wt% GO			2.5 wt% GO)		5 wt% GO		
SDS	Conversion	Particle	PDI	Conversion	Particle	PDI	Conversion	Particle	PDI	Conversion	Particle	PDI
(wt%)		<i>d</i> i (nm)			<i>d</i> i (nm)			<i>d</i> i (nm)			<i>d</i> i (nm)	
0	15	207	1	43	547	0.9	24	638	0.7	51	991	0.7
0.25	63	113	0.33	65	114	1	89	386	1	70	1017	0.2
0.5	75	96	0.4	77	1843	0.6	92	77	0.8	77	85	1
1	84	104	0.07	83	404	1	93	267	0.2	99	304	0.8

Table S3. Number-average (M_n), weight-average (M_w) molecular weights and dispersity (D) data for miniemulsion polymerization of St/nBA at 70 °C at different concentrations of SDS and GO (small and large).

	LARGE GO SHEETS						SMALL GO SHEETS					
	2.5 wt% G	0		5 wt% GO			2.5 wt% G	iO		5 wt% GO		
SDS	M _n	M _w	Ð	M _n	M _w	Ð	M _n	M _w	Ð	M _n	M _w	Ð
(wt%)	(kg/mol)	(kg/mol)		(kg/mol)	(kg/mol)		(kg/mol)	(kg/mol)		(kg/mol)	(kg/mol)	
0	26.7	58.1	2.2	21.8	38.8	1.8	5.7	11.9	2.1	9.0	21.4	2.4
0.25	36.8	115.6	3.1	31.7	105.8	3.3	16.0	51.8	3.2	16.7	49.5	2.9
0.5	32.4	128.4	3.9	18.9	91.4	4.8	20.2	59.1	2.9	82.5	214.8	2.6
1	41.4	162.0	3.9	23.1	146.6	6.3	21.2	69.5	3.3	32.2	101.4	3.2



Scheme S1. Schematic depiction and SEM images of the proposed nucleation mechanisms (type i – iv) involved in the miniemulsion polymerization of St/GO in the presence of SDS. All scale bars: 0.5 μ m. The SEM images depict the corresponding St/GO miniemulsion polymerization taken from our previous publication (reprinted with permission from ref 3. Copyright Royal Society of Chemistry 2018).³



Figure S1. SEM images of AIBN-initiated miniemulsion polymerization of St/nBA at 70 °C for 24 h with large 2.5 wt% (A0-3; red frame), large 5 wt% (B0-3; blue frame), small 2.5 wt% (C0-3; green frame), and small 5 wt% (D0-3; orange frame) GO rel. to monomer at SDS concentrations 0 (A0, B0, C0, D0), 0.25 (A1, B1, C1, D1), 0.5 (A2, B2, C2, D2), and 1 wt% (A3, B3, C3, D3) relative to organic phase. All scale bars: 5 μm (recipes A0-3, B0-3, C0-3 and D0-3 in Table S1).

Table S4. Glass transition temperatures (T_g) of nanocomposites prepared by miniemulsion polymerization of St/nBA at 70 °C with large 2.5 wt% GO, large 5 wt% GO, small 2.5 wt% GO, and small 5 wt% GO at different concentrations of SDS determined by the Fox equation ("Theoretical") and DSC, respectively

	LARGE GO SI	HEETS			SMALL GO SHEETS			
	2.5 wt% GO		5 wt% GO		2.5 wt% GO		5 wt% GO	
SDS (wt%)	τ _g (°C) Theoretical	τ _g (°C) DSC	τ _g (°C) Theoretical	τ _g (°C) DSC	T_{g} (°C) Theoretical	τ _g (°C) DSC	T_{g} (°C) Theoretical	τ _g (°C) DSC
0	3	2	6	17	2	12	6	4
0.25	3	19	6	15	4	14	8	8
0.5	5	10	5	2	3	10	8	5
1	2	21	2	4	2	8	2	10



Figure S3. Optical microscope images of nanocomposites (after reduction) prepared by AIBN-initiated miniemulsion polymerization of St/nBA at 70 °C for 24 h with large 2.5 wt% (A0-3; red frame), large 5 wt% (B0-3; blue frame), small 2.5 wt% (C0-3; green frame), and small 5 wt% (D0-3; orange frame) GO rel. to monomer at SDS concentrations 0 (A0, B0, C0, D0), 0.25 (A1, B1, C1, D1), 0.5 (A2, B2, C2, D2), and 1 wt% (A3, B3, C3, D3) relative to organic phase. (recipes A0-3, B0-3, C0-3 and D0-3 in Table S1). All scale bars: 1mm

Table S5. Average water contact angle measurements for nanocomposite films prepared by miniemulsion polymerization of St/nBA with 5wt% GO (small and large) and 0/1 wt% SDS at 70 °C before and after reduction. Data are representative of average contact angle measurements for 2 individual films and 4 measurements per film ± standard deviation (SD).

	LARGE GO SHE	ETS	SMALL GO SHEETS		
SDS (wt%)	Unreduced	Reduced	Unreduced	Reduced	
0	40°±2°	67°±3°	57°±3°	71°±4°	
1	32°±2°	65°±3°	47°±3°	66°±4°	

Table S6. Average electrical conductivity results of the nanocomposites films prepared by miniemulsion polymerization of St/nBA at 70 °C at different concentrations of SDS and GO (small and large). Data are representative of average conductivity results of 2 individual films and 3 measurements per film ± SD. Electrical conductivity values are presented in units of S/m.

	LARGE GO SHEETS		SMALL GO SHEETS	
SDS (wt%)	2.5 wt% GO	5 wt% GO	2.5 wt% GO	5 wt% GO
0	4.16x10⁻² ± 0.006	1.03x10⁻¹ ± 0.009	5.19x10⁻² ± 0.002	4.63x10⁻¹ ± 0.04
0.25	1.61x10⁻² ± 0.0008	4.03x10⁻¹ ± 0.02	1.75x10⁻² ± 0.0005	2.37x10⁻¹ ± 0.004
0.5	4x10⁻² ± 0.002	1.43 ± 0.09	2.8x10⁻² ± 0.002	7.48x10⁻¹ \pm 0.04
1	5.62x10⁻² ± 0.007	1.37 ± 0.08	4.97x10⁻² ± 0.002	2.12x10⁻¹ ± 0.01

Table S7. Thickness of the nanocomposite films prepared by miniemulsion polymerization of St/nBA at 70 °C at different concentrations of SDS and GO (small and large). The difference observed in thickness between the different films can be attributed to surface tension differences. Thickness values are presented in units of cm.

	LARGE GO SHEET	S	SMALL GO SHEETS		
SDS (wt%)	2.5 wt% GO	5 wt% GO	2.5 wt% GO	5 wt% GO	
0	0.0015	0.0092	0.0019	0.0003	
0.25	0.0029	0.002	0.0027	0.0031	
0.5	0.0020	0.0019	0.0035	0.0023	
1	0.0014	0.0026	0.0013	0.0039	

Table S8. Mass ratios of rGO (relative to total mass of nanocomposite film) in the nanocomposites prepared by miniemulsion polymerization of St/nBA at 70 °C at different concentrations of SDS and GO (small and large GO).

	LARGE GO SHEI	ETS	SMALL GO SHEETS			
SDS (wt%)	2.5 wt% GO	2.5 wt% GO 5 wt% GO		5 wt% GO		
	rGO wt%	rGO wt%	rGO wt%	rGO wt%		
0	6.1	5.1	4.3	4.4		
0.25	1.9	3.6	1.4	3.3		
0.5	1.6	3.0	1.3	3.0		
1	1.4	2.8	1.3	2.4		



Figure S4. Size distributions of small and large GO sheets; $d_n =$ number average size.

References

- 1. T. G. Fox, Bull Am Phys Soc, 1956, **1**, 123-135.
- 2. S. Sasaki and A. R. Sentā, *Handbook of Proton-NMR Spectra and Data*, Academic Press, 1985.
- 3. Y. Fadil, F. Jasinski, T. Wing Guok, S. C. Thickett, H. Minami and P. B. Zetterlund, *Polymer Chemistry*, 2018, DOI: 10.1039/C8PY00667A.