

Supporting Information for:

## Polymerizations in Oil-in-Oil Emulsions using 2D Nanoparticle Surfactants

A Bradley J. Rodier, Al de Leon, Christina Hemmingsen, and Emily Pentzer

**Materials and Instrumentation.** Glycerol was purchased from BASF ethylenediamine was purchased from Acros; all other reagents and solvents were purchased from Sigma Aldrich and used as received.

Fourier transform infrared (FTIR) spectra were obtained on an Agilent Cary 630 FTIR in ATR mode. X-ray photoelectron spectroscopy (XPS) was performed using a PHI Verasprobe 5000 spectrometer with Al K $\alpha$  radiation and internal SiO<sub>2</sub> was used as the reference. Scanning electron micrograph (SEM) images were taken with FEI Helios Nanolab 650 using Through Lens Detector (TLD) - SE mode 2 with 1 kV 25pA. Sonication was performed using an Emerson Industrial Branson Ultrasonic Bath M series 3800 model. Photochemical polymerizations were performed using a Rayonet RPR-100 Photochemical reactor (365 nm). Optical microscopy and images were performed using an AmScope microscope.

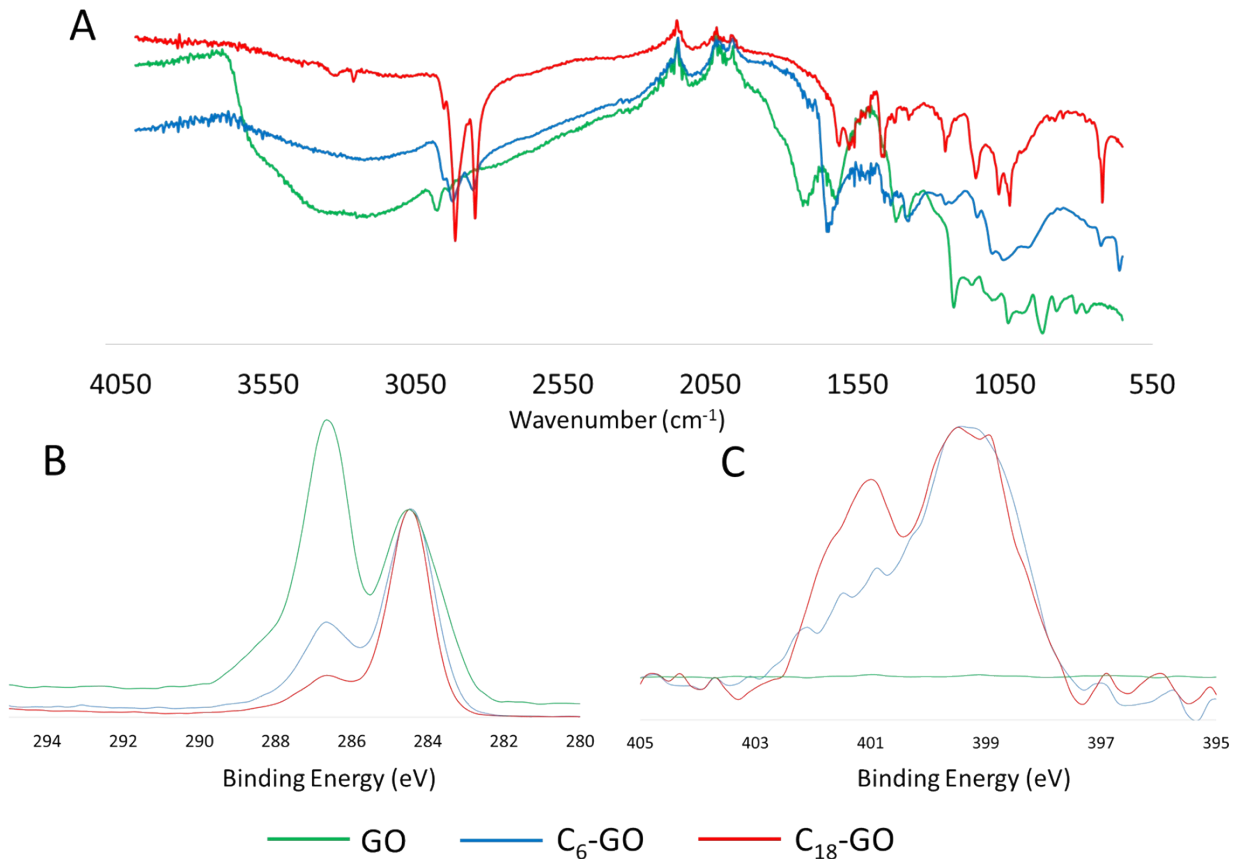
**Graphene oxide synthesis and functionalization:** The procedures used for both GO synthesis and functionalization can be found our previous work.<sup>1</sup>

**Polythioether foam synthesis:** A solution of C<sub>6</sub>-GO and DMF (~0.25 mg/ml, 500  $\mu$ l) was combined with pentaerythritol tetrakis (3-mercaptopropionate) (PTMP) (2.3 g, 4.7 mmol), 1,7-octadiyne (0.5 g, 4.7 mmol), and hydroxycyclohexyl phenyl ketone (HPK) (25 mg, 0.12 mmol) which constituted the polar, continuous phase. The non-polar, discontinuous phase consisted of hexadecane (100  $\mu$ l) and dodecane (500  $\mu$ l). After the two phases were combined into one vial, the solution was then vortexed for ~45 seconds to form a stable emulsion. The resulting emulsion was then placed in the photo reactor and irradiated for 25 minutes leading to a solid structure. The resulting material was then soaked in acetone for 3 days, replacing solvent every 24 hours. The foam was stored in acetone.

**Hollow capsule synthesis:** The polar discontinuous phase consisted of ethylenediamine (50  $\mu$ l), glycerol (500  $\mu$ l) and DMF (200  $\mu$ l). The non-polar, continuous phase contained C<sub>18</sub>-GO (0.25 mg/ml) in dodecane (3 ml) which was then emulsified through vortex mixing for 45 seconds. The emulsion formed was allowed to equilibrate for 10 minutes before 1,6-diisocyanatohexane (300  $\mu$ l, 1.87 mmol) in dodecane (200  $\mu$ l) was added dropwise to the emulsion. The reaction was allowed to run for 24 hours at room temperature. The product was isolated through washing with isopropanol and gentle stirring followed by decantation twice. The product was then washed with water in a similar manner twice.

**Polymer particle synthesis:** The polar, discontinuous phase consisted of 2-isocyanatoethyl methacrylate (0.27 g, 1.77 mmol), azobisisocyanobutyronitrile (15 mg, 0.09 mmol) and DMF (500  $\mu$ l). The non-polar, continuous phase contained C<sub>18</sub>-GO (0.25 mg/ml) in dodecane (3.5 ml). The immiscible solutions were combined and degassed through nitrogen bubbling for  $\sim$ 15 minutes. The solutions were then vortexed for  $\sim$ 45 seconds, forming a stable emulsion which was then heated at 55  $^{\circ}$ C for 18 hours. The resulting solid was then washed five times with THF and centrifugation (supernatant discarded each time, then passed through a 180 micron mesh and a beige powder was isolated.

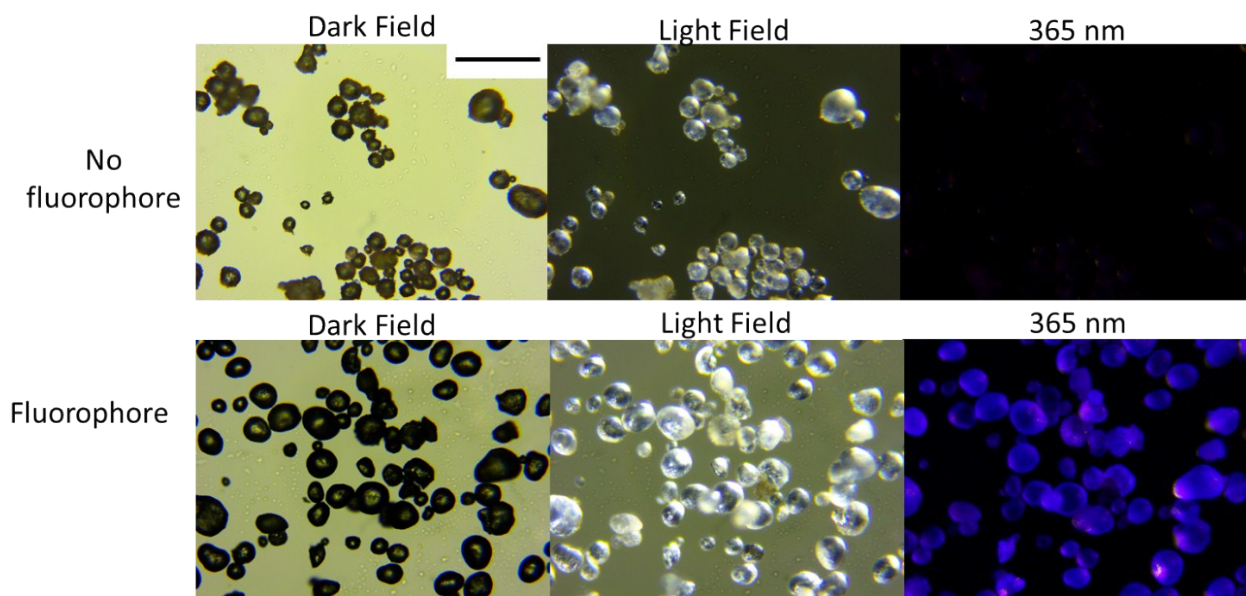
**Polymer particle functionalization:** The isolated polymer particles (20 mg) were suspended in THF (5 ml) and stirred using a magnetic stir bar. Then, a solution of 7-mercapto-4-methylcoumarin (35 mg, 0.53 mmol) and *N,N*-diisopropylethylamine (25  $\mu$ l, 0.135 mmol) in THF (5 ml) was added to the stirring suspension and allowed to react at room temperature for 10 hours. The particles were isolated by centrifugation and washed with THF six times (supernatant was discarded).



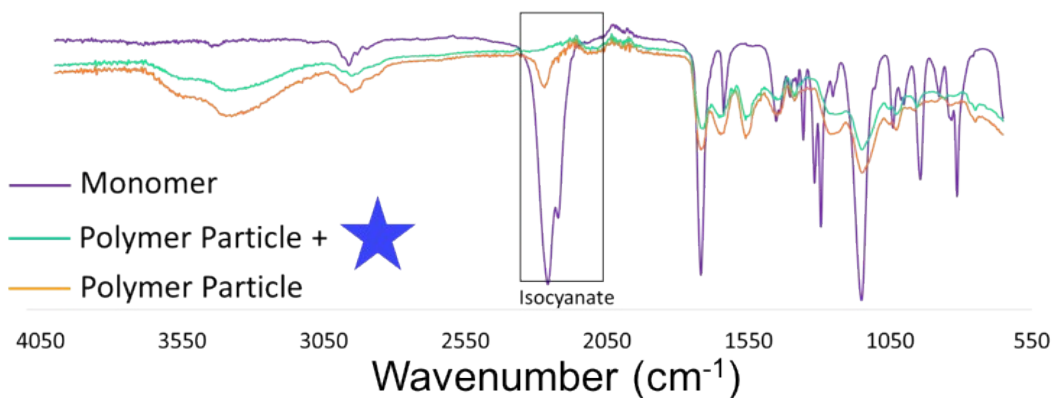
**Figure S1.** Characterization of GO (green traces), C<sub>6</sub>-GO (blue traces), and C<sub>18</sub>-GO (red traces): A) FTIR spectra; B) High resolution C 1s XPS spectra; and C) High resolution N 1s XPS spectra.

In the FTIR spectra, GO contains a broad peak at 3800-3100 cm<sup>-1</sup> indicative of the O-H bond of carboxylic acid and hydroxyl functionalities, as well as peaks at 1750 cm<sup>-1</sup> and 1600 cm<sup>-1</sup>,

indicative of C=O and C=C bonds, respectively. The FTIR spectra of C<sub>6</sub>-GO and C<sub>18</sub>-GO both show the stretching frequency corresponding to aliphatic C-H bonds from 3000-2900 cm<sup>-1</sup>, as well as signals due to C-C bonds, increasing in intensity with longer alkyl chain length. For the functionalized GO nanosheets, stretching frequencies at 1650 cm<sup>-1</sup> and 1550 cm<sup>-1</sup> are also present, indicative of carboxylates and ammonium groups respectively, and indicative of non-covalent modification.<sup>2-5</sup> XPS also verified these results, as seen in both high resolution C1s and N1s scans. In C1s, GO has well established peaks indicating C=O (288 eV), C-O (286 eV), and C-C (284 eV).<sup>6</sup> The ratio of C-O/C=O to C-C is shown to decrease as the material is functionalized by longer chains. This is representative of the reduction that occurs as the GO is functionalized as well as the introduction of increasing C-C bonds with increasing alkyl length. Additionally, in the N1s scan, GO shows no nitrogen but peaks for both ammonium (400-401 eV) and covalent amines (398-400 eV) in the reacted batch for both C<sub>6</sub> and C<sub>18</sub> variants.



**Figure S2.** Optical microscopy images of polymer particles that are unfunctionalized (top) and functionalized (bottom) with 7-mercapto-4-methylcoumarin. The reference bar is 200  $\mu\text{m}$  and applies to all images.



**Figure S3.** FTIR spectra of prepared polymer particles (orange), 2-Isocyanatoethyl methacrylate (purple trace), and polymer particles functionalized with the coumarin derivative (green). Isocyanate peak at  $\sim 2200\text{ cm}^{-1}$  indicates water sensitive functional groups survive polymerization in the emulsion.

## References

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