Supporting information for:
Inter-capsule Fusion and Capsule Shell Destruction using Dynamic Covalent Polymers
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Materials and instrumentation. Graphite, sulfuric acid (H₂SO₄), potassium permanganate (KMnO₄), N,N-Dimethylformamide (DMF, anhydrous, 99.8%), propylamine (98%), ethylenediamine (EDA, 99%+) and dibutyltin diacetate were all bought from Sigma Aldrich. Hydrogen peroxide (H₂O₂, 30%), isopropanol, toluene, triethanolamine (TEA, 98%), tetra(ethylene glycol) (TEG, 99%), 1,3-Bis(isocyanatomethyl)cyclohexane (1,3-RDI, 99%+), and hexylamine (99%) were all purchased from Fisher Scientific. Octane, dodecane, and 1-octadecyl amine were purchased from Oakwood Chemical. 1,3-Bis(2-isocyanato-2-propyl)benzene (1,3-ArDI, 97%+) was purchased from VWR. N,N-diisopropyl ethylenediamine (DIEDA, 97%) was purchased from TCI Chemical. All reagents were used as received, without purification.

Vortexing was achieved using a Fisherbrand vortex, model 9454FIALUS. Sonication was accomplished by a Fisherbrand (model CPX 3800) ultrasonic bath. Centrifugation was completed by employing a Thermo Scientific centrifuge (model 75005703). The optical microscopy images were taken by an AmScope microscope purchased from Amazon. Hand-held emulsifier (model 985370) used for emulsification was purchased from BioSpec Product Inc. Blending was carried out using a lab blender purchased from Waring Commercial, model 7010S. FTIR characterization was achieved by FTIR-4600LE Mid-IR spectrometer purchased from JASCO. TGA characterization was performed using TA Instruments TGA 5500 in the Soft Matter Facility at Texas A&M University. SEM images were taken by a Tescan Vega instrument in Microscopy and Imaging Center at Texas A&M University.

Preparation of graphene oxide (GO). Graphene oxide (GO) was prepared through the oxidation of graphite flakes by potassium permanganate (KMnO₄) and sulfuric acid (H₂SO₄) based on previously reported methods;¹⁻³ graphite flakes (3.0 g) were suspended in H₂SO₄ (400 mL) and the mixture stirred at 25 ºC, then four batches of KMnO₄ (3.0 g per batch) were added slowly to the mixture every 24 hrs. After the final batch of KMnO₄ was added and reacted for 24 hours, the resultant purple mixture was slowly and carefully added to 2.0 L of ice water with a glass rod continuously stirring at the same time. After finishing the cooling process, H₂O₂ was added to the mixture drop-by-drop and immediately stopped at the moment where the color of the mixture faded. The solid was washed by isopropanol through centrifugation until the pH was nearly neutral as tested by litmus paper. Resultant brown color precipitate was dried in a vacuum oven, then the dried product was blended to a fine powder using a
blender. GO powder was stored in the fridge to prevent reduction. The black curve in
Figure S2 shows the FTIR spectrum of GO. The broad peak ranging from 3700 cm\(^{-1}\) to
2900 cm\(^{-1}\) is attributed to the \(-OH\) group and the peaks at 1617 cm\(^{-1}\), 1721 cm\(^{-1}\) and
1230 cm\(^{-1}\) represents the C=\(\text{C}\) double bond, C=O and the C-O of epoxy, respectively.\(^4\)\(^5\)

**Preparation of C\(_{18}\)-GO.** The GO powder (96 mg) was dispersed in DMF (36 mL)
where the dispersing process was assisted by sonication. At the same time, 1-octadecyl
amine (900 mg) was dissolved in DMF (60 mL) assisted by stirring using a stir bar and
heating at 60 °C. The GO/DMF dispersion and amine/DMF solutions were combined then
heated (55 °C) and stirred for 30 mins, after which the mixture was centrifuged and
precipitated and redispersed in toluene (96 mL) with another batch of 1-octadecyl amine (2.7 g)
added. The redispersed mixture was heated (55 °C) and stirred overnight, followed by washing
with toluene and octane for two times (solid collected by centrifugation). After washing, the dark brown solid precipitate was
dispersed in 48 mL octane to prepare C\(_{18}\)-GO/octane dispersion (2 mg/mL
standardized by parent-GO). The FTIR spectrum of C\(_{18}\)-GO shows intense peaks at
2916 cm\(^{-1}\) and 2846 cm\(^{-1}\), which indicate the presence of C-H of the alkyl chain.
Besides, the peak at 1545 cm\(^{-1}\) as well as the non-obvious peak which may blend with
the C-H at around 3000 cm\(^{-1}\) illustrate the existence of N-H from the formation of
covalent bonds and amine salts between GO and 1-octadecyl amine (Figure S2).\(^2\)\(^3\)

**Synthesis of capsules.** Taking the 1,3-ArDI X DIEDA capsule as an example, the
capsule synthesis procedure was as follows. 160 µL (0.0007 mol) of 1,3-Bis(2-
isocyanato-2-propyl)benzene (1,3-ArDI), 7.6 µL (0.000058 mol) of triethanolamine
(TEA) and 68 µL (0.0004 mol) of tetra(ethylene) glycol (TEG) were first dissolved in
400 µL anhydrous DMF (dispersed phase), followed by the addition of 2 mL C\(_{18}\)-
GO/octane dispersion (continuous phase), where TEA and TEG were employed as
chain extender. The two phases were homogenized by the hand-held emulsifier for 20
s which led to the formation of DMF-in-octane emulsions, where the droplet sizes are
ranging from 10 µm to 20 µm. 42 µL (0.00023 mol) of N,N-diisopropyl ethylenediamine
(DIEDA) was dissolved in 500 µL octane assisted by heating to 40 °C and then cooled
to room temperature. The diamine/octane solution was then added dropwise to the
emulsion with hand swirling at the same time. After that, 500 µL of octane was added
to the mixture in order to dilute the system, followed by an addition of 0.7 µL dibutyltin
diacetate (catalyst). The reaction system was put in fridge for 5 days for complete
interfacial polymerization. The low temperature condition was to keep temperature-
controlled experiments and prevent undesired bond exchange. Resultant reaction
system was quenched by adding 2 mL propylamine and stored in fridge for 2 hrs,
followed by gravity filtration and washing with hexanes until the eluent was neutral, as
tested by litmus paper. Capsules were dried using reduced pressure at 5 °C. Dry
capsule powder was redispersed in dodecane to prepare samples for optical
microscopy. A similar process was used to prepare 1,3-RDI X DIEDA capsules, with
1,3-RDI used instead of 1,3-ArDI.

**Capsule fusion and destruction.** Capsules were compacted together during the
solvent evaporating process in a vial. Vials containing 30 mg compacted capsules
were then put in an oil bath (50 °C) overnight. The resultant monolith was taken out
using a spatula and observed by SEM. As for the capsule destruction, 30 mg of the dry capsule powder was redispersed in 2 mL octane assisted by vortex, followed by addition of 400 µL hexylamine and the mixture was heated in an oil bath (50 ºC) for two days. One drop of the liquid mixture was taken out by a pipette and observed under optical microscope.

**SEM sample preparation.** A SEM stub (Ø 12.7 mm sample stub w/ 3.2 mm pin) was covered by a 12 mm x 5 mm conductive carbon tape on the top surface, followed by an approximately 10 mm x 5 mm monolith sample put onto the tape. The sample was then coated with 20 nm-thick Au through a Cressington 108 Sputter Coater.

**Reference experiment.** In order to confirm the dynamic property of the HUB-bearing capsules, capsules bearing non-hindered urea bonds formed from 1,3-Bis(2-isocyanato-2-propyl)benzene (1,3-ArDI) and ethylenediamine (EDA) were prepared ([Figure S5A](#)). The synthesis procedure was similar to the process discussed in the synthesis of capsules section with N,N-diisopropyl ethylenediamine (DIEDA) changed to ethylenediamine (EDA). And based on the solubility, EDA was dissolved in DMF (dispersed phase) together with TEG and TEA, and 1,3-ArDI was dissolved in the octane to prepare diisocyanate/octane solution in this case. It is obvious that capsules are still in individual capsule state after capsule-compacted heating ([Figure S5B](#)) and emulsion system doesn’t form ([Figure S5C](#)) after primary amine addition compared to the capsules bearing HUB bonds ([Figure 3](#)).

![Figure S1](#). Hindered polyurea chemistry for the hindered poly(urea-urethane) shell of capsules. Other components of the shell have been omitted for clarity.
Figure S2. Offset FTIR spectra of GO (black curve) and C\textsubscript{18}-GO (red curve).

Figure S3. Optical microscopy images of (A) DMF-in-octane emulsion stabilized by C\textsubscript{18}-GO formed through hand-held emulsification; (B) DMF-in-octane emulsion stabilized by C\textsubscript{18}-GO formed through stirring.
Figure S4. Dry powder of (A) 1,3-Bis(2-isocyanato-2-propyl)benzene $N,N'$-diisopropyl ethylenediamine capsules; and (B) 1,3-Bis(isocyanatomethyl)cyclohexane $N,N'$-diisopropyl ethylenediamine capsules.

Figure S5. 1,3-ArDI-EDA capsules: (A) Optical microscopy image of capsules dispersed in dodecane; (B) Optical microscopy image of capsules dispersed in dodecane after heating the compacted capsules; (C) Optical microscopy image of capsules after capsule destruction by hexylamine. Inset images are photographs of the samples.
Figure S6. Dry powder of 1,3-Bis(2-isocyanato-2-propyl)benzene × ethylenediamine capsules.

References