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Dynamic Covalent Polymers**

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Inter-capsule Fusion and Capsule Shell Destruction using Dynamic Covalent Polymers

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Abstract

Herein, capsule shells containing hindered urea bonds were prepared using interfacial polymerization in an oil-in-oil Pickering emulsion stabilized by functionalized graphene oxide nanosheets. After isolation and mild heating, the polymer shells can be fused into monoliths or destroyed. These dynamic polymer shells provide a route to control the morphology of composite materials with application in energy storage, separations, additive manufacturing, controlled release, and so on.

Introduction

Capsules are structures composed of a shell of one material with or without a different material inside- filled or hollow capsules, respectively.¹⁻³ These structures have been used to improve handling of viscous liquids,⁴⁻⁶ can serve as microreactors^{5, 7, 8} and can enhance surface area of active material⁹ and thereby find application in energy storage,^{9, 10} separations,¹¹⁻¹⁵ catalysis,^{5, 6} controlled release,^{8, 16, 17} depending on the capsule composition. The most common techniques for capsule preparation are microfluidics, the hard template method (growth of shell on a solid particle followed by dissolution of the core), and interfacial reactions using an emulsion as template (i.e., soft template method). Of these, the most widely used approach is the soft template method. For example, Savin and coworkers successfully prepared hollow capsules with amphiphilic shells of cross-linked polycaprolactone-b-poly(ethylene glycol) which showed good hydrocarbon uptake efficiency.¹⁸ Likewise, our group has prepared capsules with a core of ionic liquid and composite shell of graphene oxide and polyurea for use in energy storage,¹⁰ oil remediation,¹⁹ and CO₂ uptake.^{11, 14}

The chemical composition of capsule shells is critical to application-oriented properties such as mechanical strength,²⁰⁻²² porosity,²¹⁻²⁴ chemical stability and reactivity,^{25, 26} and electrical and thermal characteristics,^{10, 23, 26, 27} as well as shape.^{22, 28} For example, Nascimento and colleagues prepared polydimethylsiloxane shells where the elasticity was tuned by adjusting the amount of crosslinker.²⁰ Likewise, Pisani *et al.* fabricated shells of poly(lactide-co-glycolide) (PLGA) and poly(lactide-co-glycolide)-polyethylene glycol (PLGA-PEG)²⁸ where the surface morphology was controlled by the ratio of the polymers. Alternatively, Zhang *et al.* used imine condensation to prepare capsule shells of covalent organic frameworks (COFs), then attached gold

particles which had pendant amines to the shell.²⁹ In a similar vein, Hatai *et al.* prepared polymer shells containing hydrazone units and coumarin dimers which released the contents of the capsule core in response to changes in pH, light irradiation, or the presence of metal ions.³⁰ Thus, integration of chemical functionalities that can undergo reactions under relatively mild conditions can be used to tailor properties.

Dynamic covalent bonds (DCBs) are those which can reversibly break and form under mild conditions or external stimuli.^{31, 32} Polymers containing these bonds have promising application in self-healing,³³⁻³⁵ shape-memory,^{34, 36, 37} and sensors.³⁸ Examples of DCBs include transesterification,³⁹ amide/imine/aldol chemistry,³⁹ alkene- or alkyne-metathesis,³⁹⁻⁴¹ boronic acid condensation,⁴² Diels-Alder reactions,^{39, 43} and so on. Hindered urea bonds (HUBs) are DCBs formed by the reaction of an isocyanate with a secondary amine, the latter of which bears a bulky alkyl group, such as isopropyl or tert-butyl. The sterically demanding nitrogen substituent leads to non-planarity of the urea bond and enables the reverse reaction (urea \rightarrow amine + isocyanate) to occur under mild thermal conditions; this is in contrast to urea bonds formed from primary amines and isocyanates which are generally considered irreversible (**Figure 1** and **Figure S1**).^{44, 45} Cheng and coworkers demonstrated that polymer films bearing HUBs, those formed by reaction of multifunctional secondary amines and multifunctional isocyanates, have self-healing,⁴⁴ shape retentive,³⁷ and recyclable properties.⁴⁶

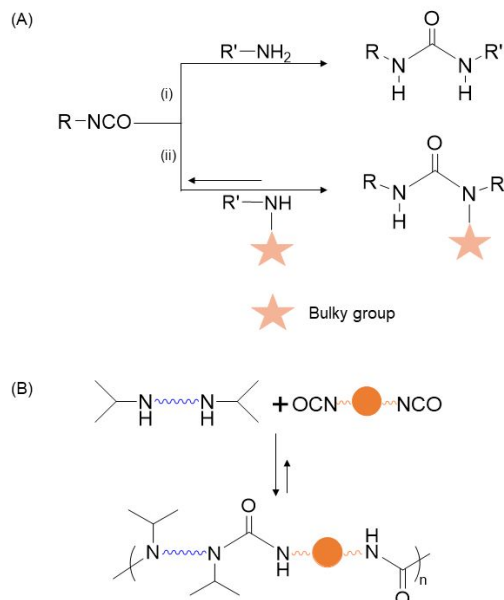
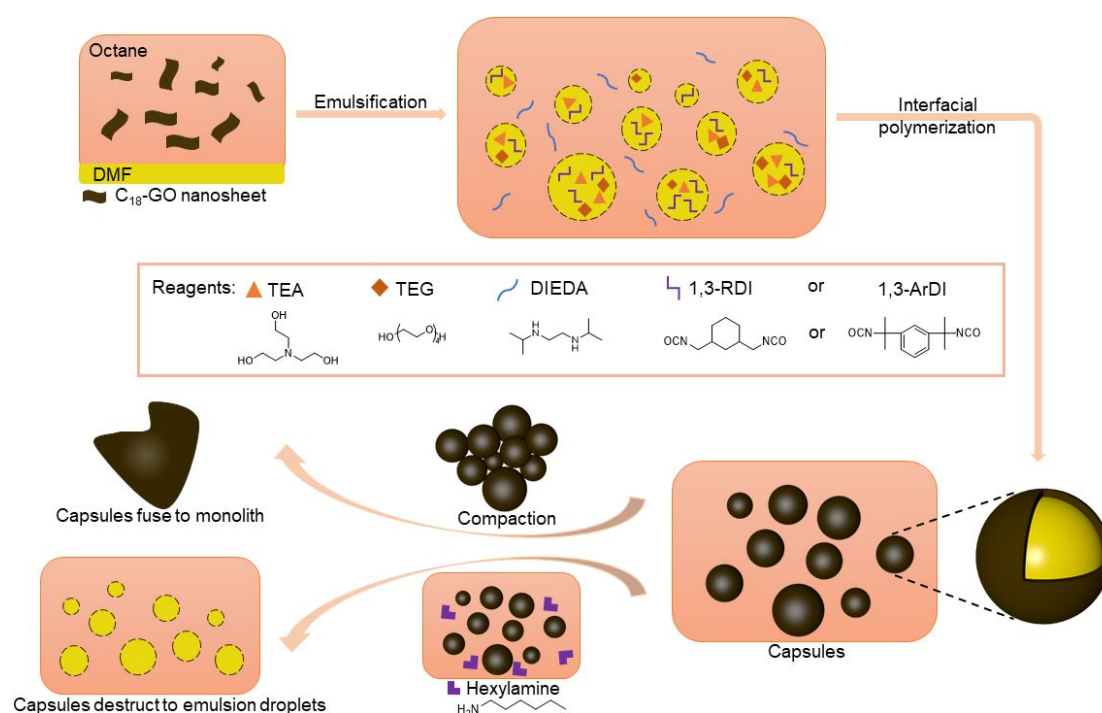


Figure 1. (A) Illustration of (i) irreversible urea bond formed by reaction of an isocyanate and primary amine, and (ii) reversible hindered urea bond (HUB) formed by reaction of an isocyanate and secondary amine bearing a bulky substituent; and (B) hindered polyurea chemistry.

Herein, we report polymer capsules with shells that incorporate HUBs and demonstrate that the presence of these bonds can be used to either fuse

capsule shells into monoliths by subjecting isolated, dried capsules to mild heating, or to destroy capsule shells by exposing them to primary alkyl amine (**Scheme 1**). The shells containing hindered poly(urea-urethanes) are prepared by interfacial polymerization in an oil-in-oil Pickering emulsion stabilized by alkylated graphene oxide (GO) nanosheets. Optical microscopy imaging is used to follow the changes in capsule morphology, whereas Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) are used to characterize the composition of the shells. The tailored capsule chemistry allows for a monolith to be prepared, in any shape and at any time, supporting liquid transport for energy storage, molecule separation, and additive manufacturing, whereas capsule destruction on demand may find use in self-healing and controlled release applications.



Scheme 1. Overview of the work reported here: formation of capsules with shells containing hindered urea bonds (HUBs) and the fusion or destruction of the capsule shells. Capsules were prepared by interfacial polymerization in oil-in-oil Pickering emulsions stabilized by functionalized graphene oxide nanosheets.

Results and Discussion

Oil-in-oil emulsions were selected as the template to prepare capsules with composite shells containing HUBs because these water-free emulsions enable control of the capsule composition; specifically, water hydrolyzes isocyanates to give primary amines and expel CO₂, then the amine can react irreversibly with other isocyanate functionalities. We leveraged alkylated graphene oxide (GO) nanosheets as particle surfactant to stabilize DMF-in-octane emulsions.

These particle surfactants were prepared as previously reported,^{19, 47} by the modification of GO with 1-octadecyl amine, giving (C₁₈-GO), as verified by FTIR spectroscopy (**Figure S2**) and changes in dispersibility. With C₁₈-GO as a particle surfactant dispersed in octane, a DMF-in-octane emulsion was prepared using a hand-held emulsifier (**Figure S3A**); even without interfacial polymerization, these emulsions were stable for at least ten days.

To prepare capsules with shells containing HUBs, a diisocyanate, triethanolamine, and tetra(ethylene glycol) were dissolved in DMF before emulsification, then an octane solution of *N,N*-diisopropyl ethylenediamine (DIEDA) and dibutyltin diacetate was added to the continuous phase. Triethanolamine and tetra(ethylene glycol) were used as polymer chain extenders, consistent with the work of Cheng.⁴⁴ Two different diisocyanates were used, the primary isocyanate 1,3-Bis(isocyanatomethyl)cyclohexane (1,3-RDI) and tertiary isocyanates 1,3-Bis(2-isocyanato-2-propyl)benzene (1,3-ArDI), as they may have different rates of reactions with secondary amines. After emulsification and addition of all reagents, the emulsions were left unagitated for 5 days, then propylamine was added to quench any unreacted isocyanates and prevent undesired inter-capsule fusion. Dry powders of the capsules (**Figure S4**) were isolated by gravity filtration, dried under reduced pressure, and could be dispersed in dodecane. Of note, during preparation and isolation, the samples were kept at 5 °C for consistency across studies.

The optical microscopy images in **Figure 2A and 3A** show that nearly-spherical, individual capsules of 1,3-RDI-DIEDA and 1,3-ArDI-DIEDA were obtained. Upon isolation, some of the inner oil phase may be removed, and thus the wrinkled morphology can be attributed to changes in the internal volume. For 1,3-RDI-DIEDA, most of the capsules range from 25 μm to 45 μm, with some smaller capsules between 5 μm and 10 μm also present. Most of the 1,3-ArDI-DIEDA capsules are slightly smaller and approximately 20-30 μm with a few smaller ones are also around 10 μm. This slight difference of capsule size range may be attributed to the use of different diisocyanate monomers, which can lead to different rates of crosslinking and shell thickness (our group is investigating this phenomenon further). The FTIR spectra of the monomers and capsule shells are shown in **Figure 4**, demonstrating the successful formation of polyurea. For both capsule shells, there is no peak corresponding to the N=C=O of the isocyanate (~2241 cm⁻¹), and the stretching and bending frequencies at 3314 cm⁻¹ and 1534 cm⁻¹ support formation of N-H, whereas the stretching frequency at 1700 cm⁻¹ supports formation of the urea carbonyl. Characterization of the capsules by thermogravimetric analysis (TGA) is shown by the weight loss profiles in **Figure 5**. For both capsules, the majority of weight loss occurred between 210 °C and 400 °C, which can be attributed to the polymer; the minor weight loss below 100 °C is consistent with the bulk polymer⁴⁸ and may be due to solvent evaporation or by reaction of adsorbed water with thermally liberated isocyanates which would cause loss of gaseous CO₂.

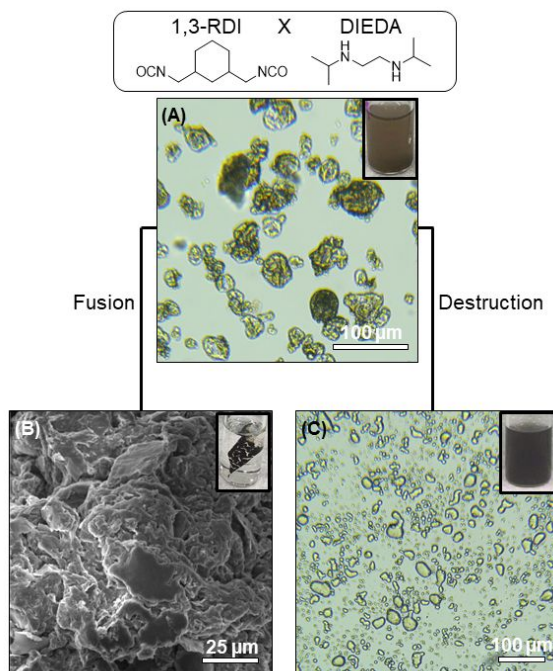


Figure 2. 1,3-RDI-DIEDA capsules: (A) Optical microscopy image of capsules dispersed in dodecane; (B) SEM image of monolith after capsule fusion; (C) Optical microscopy image of droplets after capsule destruction by hexylamine. Inset images are photographs of the samples.

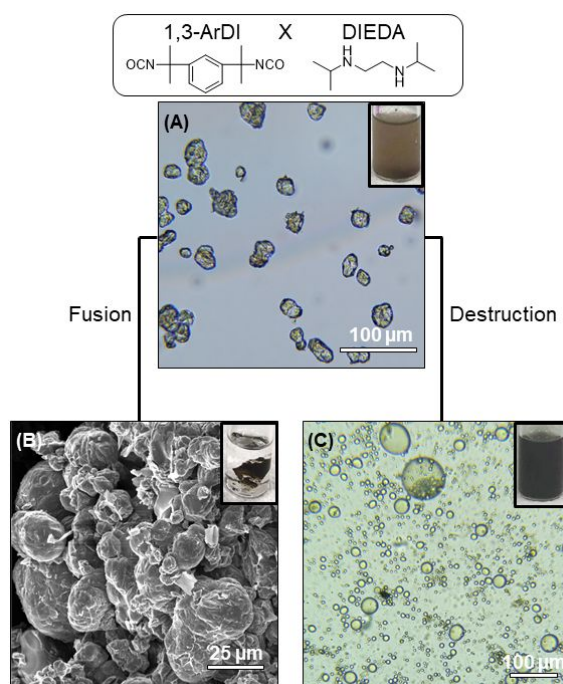


Figure 3. 1,3-ArDI-DIEDA capsules: (A) Optical microscopy image of capsules dispersed in dodecane; (B) SEM image of monolith after capsule fusion; (C) Optical microscopy image of droplets after capsule destruction by hexylamine. Inset images are photographs of the samples.

The ability of the DCBs in the polymer shell to either fuse the capsule shells into monoliths or destroy the polymer component of the shell was then evaluated. Fusion of capsule shells requires them to be in close contact with each other, which was achieved by compacting the capsules during the drying process, as solvent evaporated. The compacted capsules were placed in a vial that was heated at ~ 50 °C overnight, resulting in formation of a monolith for both capsule systems, as shown in **Figures 2B** and **3B**. This capsule shell fusion is attributed to bond exchange between the polymers of the neighboring capsules based on the reversible nature of the HUBs. The inset pictures of **Figure 2B** and **3B** further illustrate the formation of a monolith. Subjecting capsules that do not contain HUBs (i.e., were prepared using a primary diamine) to the same conditions did not lead to monolith formation, but the capsules remained dispersible in dodecane (**Figures S5** and **S6**).

The polymer component of the shell can alternatively be destroyed in the presence of a primary amine at an appropriate temperature. Reversion of the HUB gives a secondary amine and an isocyanate, the latter of which undergoes irreversible reaction with the primary amine. To destroy the polymer component of the capsule shells, isolated capsules were dispersed in octane, then hexylamine was added and the mixture heated to 50 °C. The optical microscopy images in **Figures 2C** and **3C** show that the capsule shells were destroyed, as indicated in the change in contrast, with the system reverting to the emulsion. From these microscopy images, the stabilizing agent of the emulsion is unclear, and may be attributed to small molecules or oligomers produced or C_{18} -GO nanosheets. The majority of the newly-formed emulsion droplets are smaller (< 25 μm) than that of corresponding capsules, and are more similar to droplets in the DMF-in-octane emulsion templates (**Figure S3**). This supports that interfacial polymerization can lead to differences between the size of droplets and capsules. Additionally, some non-spherical droplets are observed in the 1,3-RDI-DIEDA sample after capsule destruction, which may be due to the uneven distribution of various surfactants at the fluid-fluid interface.

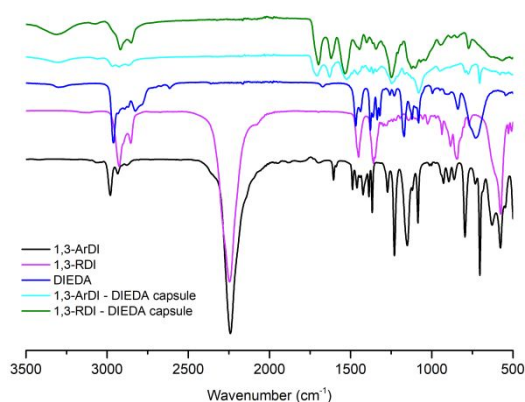


Figure 4. Offset FTIR spectra (% transmission) of the diisocyanates 1,3-ArDI (black line) and 1,3-RDI (purple line); diamine DIEDA (blue line); and capsules of 1,3-ArDI-DIEDA (light blue line) and capsules of 1,3-RDI-DIEDA (olive line).

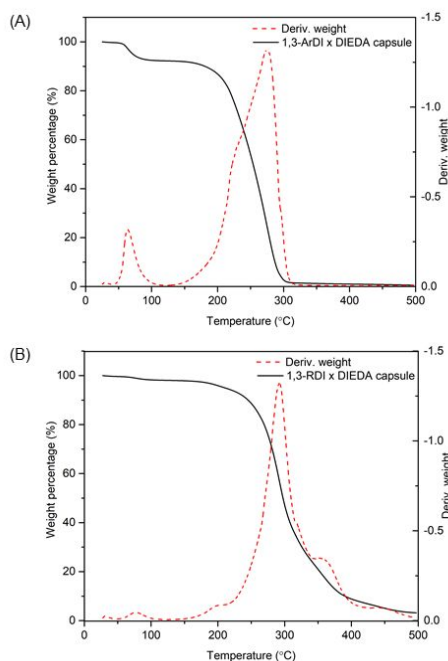


Figure 5. TGA weight loss profiles and their first derivatives of (A) 1,3-ArDI-DIEDA capsules and (B) 1,3-RDI-DIEDA capsules.

Summary

In this communication, we report the preparation of capsule shells containing hindered urea bonds (HUBs) and use them to form monoliths by shell fusion, or destroy them by addition of a primary amine. The capsules are prepared using a water-free oil-in-oil emulsion stabilized by C₁₈-GO. We demonstrate that diisopropyl ethylenediamine (DIEDA) can be used with two different diisocyanates to form these dynamic shells. Importantly, at and below room temperature, the dynamicity of the bonds within the shell is slow enough such that capsules remain intact, but a slight increase in temperature to ~50 °C enables capsule fusion or destruction, depending on the conditions used. This work provides the ability to form monoliths from dry capsule powder or destroy the shell on demand, and is expected to find use across a broad spectrum of applications. Ongoing work in our lab focuses on further tuning the polymer chemistry of the capsule shell to control the temperature at which fusion and destruction occurs, as well as incorporating other core materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at.

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Author Contributions

Y.W. and E.P. designed the experiments. Y.W. carried out the experiments with the assistance of K.Q. and performed all characterization. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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