Stabilizing and structuring oil–oil interfaces by molecular brush surfactants

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Abstract
Oil-in-oil (O/O) emulsions provide a unique platform for numerous applications not compatible with water or aqueous systems. However, the limited types and complicated synthesis process of surfactants are problematic. Here, we put forward a simple, yet powerful strategy to stabilize the oil–oil interface, then prepare oil-in-oil emulsions, by using the co-assembly of polar molecular brushes and nonpolar oligomeric ligands at the DMF–octane interface. Molecular brush surfactants (MBSs) form and assemble in situ at the interface, minimizing the interfacial energy and producing a robust film. We find that the binding energy of MBS to the interface is sufficiently high, leading to the construction of structured liquids by the interfacial jamming of MBSs. Using MBSs as emulsifiers, different types of emulsions including DMF-in-octane, octane-in-DMF, and high internal phase emulsions can be easily prepared, showing promising applications in microreactor systems and advanced composite materials.

KEYWORDS
emulsions, oil–oil interfaces, jamming, molecular brush, surfactants

1 | INTRODUCTION

Oil-in-oil (O/O) emulsions, also known as nonaqueous emulsions or anhydrous emulsions, are mixtures of two immiscible polar/nonpolar organic liquids, where one liquid is dispersed as droplets in another liquid that is the continuous phase. O/O emulsions are complementary to traditional water-in-oil (W/O) or oil-in-water (O/W) emulsions, offering an attractive platform for a number of applications not compatible with aqueous systems, for example, the encapsulation of hydrolytically unstable or poorly water-soluble active materials or the synthesis of polymer latex particles that require water-sensitive monomers or catalysts. However, in comparison to widely studied O/W and W/O emulsions, O/O emulsions have received much less attention, mainly due to the difficulty of finding or designing suitable surfactants for stabilizing the oil–oil interface. Unlike oil–water systems that have an interfacial tension of 30–50 mN m\(^{-1}\), oil–oil systems have an extremely low interfacial tension, generally 0–5 mN m\(^{-1}\). As a result, low molecular weight surfactants usually cannot be used to stabilize the oil–oil interface due to the limited reduction in interfacial tension. Also, most of the low molecular weight surfactants are slightly soluble in both oil phases that have insufficient difference in polarities to stabilize the interface and, therefore, the emulsion droplets.

In recent years, block copolymers and Pickering particles have been shown to be perfect steric stabilizers for O/O emulsions and have gained increasing attention. The amphiphaticity and solubility of block polymers can be effectively tuned by controlling parameters such as chemical composition, molecular weight, and relative block size, leading to the stabilization of specific oil–oil interfaces. Müllen and Klapper et al. used polyisoprene-\(b\)-poly(methyl methacrylate) (PI-PMMA), where PI and PMMA blocks are selectively soluble in the nonpolar and polar phases, respectively, as surfactants to stabilize either \(N,N\)-dimethylformamide (DMF)–alkane or acetonitrile–alkane emulsions, and produced polymeric particles by emulsion polymerization.

On the other hand, by modifying the surface properties of Pickering particles, the polarity and wettability of the particles can be well-controlled, leading to the preparation of different types of O/O emulsions, that is, nonpolar-in-polar or polar-in-nonpolar. Pentzer et al. have used graphene oxide (polar) modified alkyl chain (nonpolar) as surfactants to stabilize either octane–DMF or octane–acetonitrile emulsions, and demonstrated that the length of the alkyl chain dictates the continuous phase of the O/O emulsions.
Despite these achievements, the limited types and complicated synthetic processes to generate block copolymers and Pickering particles present limitations, restricting the wide application of O/O emulsions. Therefore, developing an easy and efficient way to prepare surfactants for O/O emulsions is needed.

Herein, we present a simple, yet powerful strategy to stabilize O/O emulsions by using the co-assembly of a polar molecular brush (MB), poly(2-hydroxyethyl methacrylate)-g-poly(acrylic acid) (PHEMA-g-PAA), and a nonpolar oligomeric ligand, amine-functionalized polyhedral oligomeric silsesquioxane (POSS–NH₂), at the DMF–octane interface. Molecular brush surfactants (MBSs) form and assemble in situ at the interface, minimizing the interfacial energy and producing an elastic film with excellent mechanical properties (Figure 1). By varying the mass ratio of PHEMA-g-PAA to POSS–NH₂, or the volume ratio of DMF and octane, different types of emulsions including DMF-in-octane, octane-in-DMF, and octane-in-DMF high internal phase emulsion (HIPE) can be easily prepared. Moreover, the binding energy of MBSs to the interface is sufficiently high to support the load under compression, offering the possibility of structuring liquids into nonequilibrium shapes.

2 | RESULTS AND DISCUSSION

PHEMA-g-PAA was synthesized according to the previous work. Due to the steric repulsion between densely grafted PAA side chains (~90% grafting ratio), PHEMA-g-PAA adopts a wormlike conformation with a length of several hundreds of nanometers and a diameter of ~40 nm (Figure S1). As PHEMA-g-PAA is polar and POSS–NH₂ is non-polar, they can be selectively soluble in DMF and octane, respectively. The kinetics of the MBSs formation and assembly at the DMF–octane interface was probed by pendant drop tensiometry, where the evolution of interfacial tension with time was tracked after the DMF phase was slowly injected into the octane phase to form a pendant droplet. Prior to that, the interfacial tension of different DMF–octane systems was investigated. The pure DMF–octane system has a low interfacial tension of ~3.7 mN m⁻¹ (Figure S2). With PHEMA-g-PAA dissolved in DMF against pure octane, or POSS–NH₂ dissolved in octane against pure DMF, a slightly reduced interfacial tension of ~3.2 mN m⁻¹ is obtained, as shown in Figure 2A,B, indicating that either PHEMA-g-PAA or POSS–NH₂ does not possess a sufficiently different polarity to stabilize the DMF–octane interface. This result can also be supported by squeezing two DMF droplets with only PHEMA-g-PAA dissolved in DMF phase or POSS–NH₂ dissolved in the octane phase, where the two droplets coalesce rapidly (Figure 2D,E).

With PHEMA-g-PAA dissolved in DMF against POSS–NH₂ dissolved in octane, it is found that the interfacial tension reduces to ~0.8 mN m⁻¹ rapidly within 50 s and, with time, a gradual elongation of the pendant droplet is observed. Consequently, the Young–Laplace equation is no longer valid, and the interfacial tension cannot be measured by the shape of the pendant droplet (Figure 2C). When squeezing two DMF droplets with PHEMA-g-PAA dissolved in the DMF phase and POSS–NH₂ dissolved in the octane phase, no coalescence is observed and droplets can be fully separated after contact, giving clear evidence that PHEMA-g-PAA co-assembles with POSS–NH₂ at the interface, due to the electrostatic interaction/hydrogen bonding between carboxyl groups and amine groups, generating MBSs and an elastic interfacial film (Figure 2F).

Interestingly, when contracting the droplet to compress the interfacial assemblies, wrinkles are observed on the droplet surface and do not relax (Figure 3A, Figure S3), indicating the binding energy of MBSs to the interface is sufficiently high to support load under compression, and the MBSs jam. It should be noted that wrinkles are observed only when both PHEMA-g-PAA and POSS–NH₂ are added to DMF and octane, respectively (Video S1–S4). If the droplet is fully withdrawn into the needle and then reinjected to the initial volume, a highly deformed droplet in a nonequilibrium state can be constructed (Figure 3B and Video S5). This wrinkling and jamming behaviors are similar with that observed in oil/water systems, where the interface is stabilized by nanoparticle surfactants or other
type of colloidal particles. In a jamming process, the interfacial assemblies undergo a “liquid-like” to “solid-like” transition, with significantly enhanced mechanical properties and more importantly, jamming affords the possibility to arrest interfacial tension-driven morphological variation, that is, to structure liquids. Taking advantage of the interfacial jamming of MBSs in oil/oil systems, it is highly anticipated that water-sensitive all-liquid reaction vessels and microfluidic devices can be generated. By performing an oscillating pendant drop experiment, the rheological properties of MBS-based interfacial assemblies were investigated at low concentrations. In the frequency range of 0.01–1.0 Hz, both viscous and elastic components are obtained, with elastic part being the dominant component, demonstrating the elastic nature of the interfacial assemblies (Figure S4).

The rate at which MBSs form and assemble at the interface can be estimated by tracking of the surface coverage \(S_j\) of MBSs on the droplet, which is estimated from the ratio \(S_j/S_F\), where \(S_j\) and \(S_F\) are surface areas for the jammed and free (initial) states, respectively. We note that at the point where wrinkles are observed to determine \(S_j\), it is sufficient to have a percolated pathway to produce wrinkles which does not necessarily mean that areally dense layer has formed, so \(S_j\) can only be used as an estimate. As shown in Figure 3C, MBSs form and assemble at the interface rapidly, reaching full coverage of 100% within 100 s. By varying the concentration of either PHEMA-g-PAA or POSS–NH₂, the interfacial activity and surface coverage of MBSs at equilibrium can be well-adjusted (Figure S5). Using a flat DMF–octane interface as a template, 2D macroscopic films with elasticity can be prepared, then transferred to a silicon wafer (Figure 3D). Based on atomic force microscopy (AFM) measurements, the thickness of the film is determined as \(\sim 40\) nm, close to the diameter of PHEMA-g-PAA, indicating the formation of the PHEMA-g-PAA monolayer at the interface (Figure 3E,F). This monolayer adsorption is also evidenced by measuring the thickness of a dried emulsion droplet on the substrate. Membrane with a thickness of \(\sim 80\) nm is obtained, about...
FIGURE 4  (A) The chemical structure and representation of MB-1. (B) Schematic and LSFCM images of a DMF droplet containing MB-1 surrounded by pure octane over time. (C) Schematic and LSFCM images of a DMF droplet containing MB-1 surrounded by octane solution containing POSS–NH₂ over time. (D) The chemical structure and representation of MB-2. (E) Schematic and LSFCM images of a DMF droplet containing MB-2 surrounded by pure octane over time. (F) Schematic and LSFCM images of a DMF droplets containing MB-2 surrounded by octane solution containing POSS–NH₂ over time. scale bar: 100 µm. DMF, dimethylformamide; LSFCM, laser scanning fluorescence confocal microscope; MB, molecular brush; POSS–NH₂, amine-functionalized polyhedral oligomeric silsesquioxane

FIGURE 5  LSFCM images showing different types of emulsions including (A) octane-in-DMF and (B) DMF-in-octane, with the mass ratio of PHEMA-γ-PAA to POSS–NH₂ changing from 1/1 to 0.5/20 (V₁/\text{V₂}_\text{octane} = 1/1). LSFCM images of different types of emulsions including (C) octane-in-DMF, (D) DMF-in-octane, and (E) HIPE, with the volume ratios of DMF to octane changing from 2/1 to 1/10, then to 1/3. (F,G) Storage modulus and loss modulus of HIPE as a function of strain in the oscillatory strain sweep and as a function of frequency in the oscillatory frequency sweep. From (C) to (G), [PHEMA-γ-PAA] = 1.0 mg mL⁻¹, [POSS–NH₂] = 1.0 mg mL⁻¹. DMF, dimethylformamide; HIPE, high internal phase emulsion; LSFCM, laser scanning fluorescence confocal microscope; PHEMA-γ-PAA, poly(2-hydroxyethyl methacrylate)-γ-poly(acrylic acid); POSS–NH₂, amine-functionalized polyhedral oligomeric silsesquioxane

twice that of the film prepared in a flat DMF–octane interface (Figure S6).

By functionalizing PHEMA-γ-PAA with 5-aminotetramethylrhodamine to produce MB-1 (Figure 4A, Scheme S1, Figure S7,S8), which fluoresces at ~610 nm.[41] The spatial distribution of PHEMA-γ-PAA during the assembly process can be probed by laser scanning fluorescence confocal microscope (LSFCM). As shown in Figure 4B, when placing a 10 µL droplet of a DMF solution of MB-1 into pure octane, MB-1 is uniformly distributed in the droplet and does not segregate to the interface, which is in agreement with the interfacial tension result in Figure 2A. However, with MB-1 dissolved in DMF and POSS–NH₂ dissolved in octane, enhanced fluorescence intensity is observed at the DMF–octane interface, indicating the formation and assembly of MBSs (Figure 4C, Figure S9). By
functionality of PHEMA-g-PAA with a typical aggregation-induced emission (AIE) molecule, 4-(1,2,2-triphenylvinyl)aniline, to produce MB-2 (Figure 4D, Scheme S2, Figures S10 and S11), the aggregation of PHEMA-g-PAA at the interface can be characterized. As shown in Figure 4E, with only MB-2 dissolved in DMF, no fluorescence can be observed in the droplet or at the interface, since the AIE molecules are nearly non-emissive in dilute solutions. With MB-2 dissolved in DMF and POSS–NH₂ dissolved in octane, the interface shows an enhanced fluorescence intensity with time, while the droplet shows no fluorescence, indicating the AIE molecules and, therefore, MB-2, are concentrated at the interface (Figure 4F, Figure S12). These results further demonstrate the advantage of this co-assembly strategy and the efficiency of MBSs in stabilizing the oil–oil interface.

Emulsions were prepared by vigorously homogenizing the mixture of DMF dissolving PHEMA-g-PAA and octane dissolving POSS–NH₂. We note that, with only PHEMA-g-PAA or POSS–NH₂ dissolved in DMF or octane, stable emulsions do not form. Due to the different polarities of PHEMA-g-PAA and POSS–NH₂, the polarity of MBSs, as well as the emulsion type, can be easily adjusted by varying the concentration of PHEMA-g-PAA or POSS–NH₂ in each phase. As shown in Figure 5A,B and Figures S13 and S14, at a DMF/octane volume ratio of 1/1, with the mass ratio of PHEMA-g-PAA to POSS–NH₂ changing from 1/1 to 0.5/20, octane-in-DMF and DMF-in-octane emulsions are obtained, respectively, as evidenced by the fluorescence signal of Rhodamine B in the DMF phase. In comparison to studies on block copolymers or Pickering particles for stabilizing oil-in-oil emulsions, the generation of MBSs avoids the complicated chemical synthesis or modification of block copolymers or Pickering particles, that are essential to ensure solubility of the block copolymers or Pickering particles in one specific oil phase. Moreover, by fixing the concentration of PHEMA-g-PAA and POSS–NH₂ at 1.0 mg mL⁻¹ and changing the volume ratio of DMF and octane from 2/1 to 1/10, octane-in-DMF and DMF-in-octane emulsions can also be achieved (Figure 5C,D and Figures S15 and S16). Unexpectedly, at a DMF/octane volume ratio of 1/3, octane-in-DMF HIPEs were found (Figure 5E). The rheological properties of the HIPEs, which are essential for developing practical applications, such as food processing, cosmetics, and pharmaceuticals, were investigated. As shown in Figure 5F, when applying a strain (<75%) to HIPEs, the storage modulus (G′) is higher than the loss modulus (G″), indicating an elastic or solid-like behavior of HIPEs. Over the entire range of frequencies measured (from 0.1 to 100 Hz), G′ was considerably higher than G″, suggesting good stability of HIPEs (Figure 5G).

3 | CONCLUSION

In summary, we demonstrate a facile route to stabilize the DMF–octane interface by using a newly developed MBSs, produced by the co-assembly of polar PHEMA-g-PAA and nonpolar POSS–NH₂. The in situ formation, assembly and jamming of MBSs at the oil–oil interface were investigated by pendant drop tensiometry and LSCFM. MBS behaves as an efficient surfactant, with significantly enhanced binding energy to the interface in comparison to either PHEMA-g-PAA or POSS–NH₂, allowing them to jam at the interface, and arrest change in the liquid shape. By varying the mass ratio of PHEMA-g-PAA to POSS–NH₂, the polarity of MBSs can be tuned, resulting in the preparation of either octane-in-DMF or DMF-in-octane emulsions. Moreover, octane-in-DMF HIPEs can be achieved at a specific volume ratio of DMF and octane. These types of O/O emulsions are of great interest as microreactor systems for the polymerization of water-sensitive monomers or catalysts, and as a template for the construction of tissue engineering scaffolds. This co-assembly strategy at the oil–oil interface is wide open for further exploration. The DMF/octane system could be extended to other oil/oil systems. In addition to PHEMA-g-PAA and POSS–NH₂, many functional nanomaterials, for example, nanoparticles, and ligands with complementary groups could be combined to stabilize the interface, then to prepare liquid constructs.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest that could be perceived as prejudicing the impartiality of the research reported.

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