Controlling the Size of Two-Dimensional Polymer Platelets for Water-in-Water Emulsifiers

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Supporting Information

ABSTRACT: A wide range of biorelevant applications, particularly in pharmaceutical formulations and the food and cosmetic industries, require the stabilization of two water-soluble blended components which would otherwise form incompatible biphasic mixtures. Such water-in-water emulsions can be achieved using Pickering stabilization, where two-dimensional (2D) nanomaterials are particularly effective due to their high surface area. However, control over the shape and size of the 2D nanomaterials is challenging, where it has yet not been possible to examine chemically identical nanostructures with the same thickness but different surface areas to probe the size-effect on emulsion stabilization ability. Hence, the rationale design and realization of the full potential of Pickering water-in-water emulsion stabilization have not yet been achieved. Herein, we report for the first time 2D poly(lactide) platelets with tunable sizes (with varying coronal chemistry) and of uniform shape using a crystallization-driven self-assembly methodology. We have used this series of nanostructures to explore the effect of 2D platelet size and chemistry on the stabilization of a water-in-water emulsion of a poly(ethylene glycol) (PEG)/dextran mixture. We have demonstrated that cationic, zwitterionic, and neutral large platelets (ca. 3.7 × 10^6 nm^2) all attain smaller droplet sizes and more stable emulsions than their respective smaller platelets (ca. 1.2 × 10^5 nm^2). This series of 2D platelets of controlled dimensions provides an excellent exemplar system for the investigation of the effect of just the surface area on the potential effectiveness in a particular application.

INTRODUCTION

Emulsions of oil and water can be stabilized against coalescence using various emulsifying agents, such as simple surfactants, as they strongly adsorb to oil–water interfaces due to high interfacial tensions. Recently, Pickering emulsions, where the emulsion is stabilized by particles rather than surfactants, have gained increasing interest. Indeed, inorganic colloidal particles, such as silica sols, nanocomposites, and Laponite clay platelets, as well as organic latexes and self-assembled nanoparticles, have all been reported as effective stabilizers. Recently, 2D polymer nanostructures, such as amphillic18 and Janus nanosheets,19 have found application in the formation of Pickering emulsions, although, in these examples, the emulsions are partially stabilized by the amphiphlicity of the particles as well as by a Pickering effect.

A number of applications, particularly in pharmaceutical formulations and the food and cosmetic industries, require stabilization in blending two water-soluble components which would otherwise form incompatible biphasic mixtures. For example, food products contain incompatible water-soluble mixtures such as proteins and polysaccharides.20 Such blends can be achieved using water-in-water emulsions; however, because of the ultralow interfacial tension and thickness of the interface, stabilization is difficult to accomplish using surfactants.21,22 Such stabilization can be achieved using triblock copolymers,23 polymer–protein conjugates,24 and, recently, elongated and 2D nanoparticle stabilizers have been examined for the stabilization of water-in-water emulsions,25 where it has been shown that more stable emulsions can be achieved for particles of greater aspect ratio.26,27 In particular, it was shown that the use of cellulose nanorods28 and Gibbsite nanoplates can act as efficient emulsifiers.29 However, these approaches do not offer the ability to readily modulate the chemistry, size, or shape of the construct to explore its effectiveness as a stabilizer. Indeed, despite the recent extensive interest in such ultrathin 2D materials, such as graphene, boron nitride, and clay platelets, for applications in optical devices,30 catalyst arrays,31 organic electronics32 and as templates,33 investigations into the combination of controlled particle shape and size are much less explored owing to the inability to control this further dimension in inorganic materials. Hence, we propose utilizing the precision and complexity offered by organic polymer assembly methods to create a series of nanoparticle stabilizers of tunable chemistry with controlled size and shape.

A number of techniques exist which focus on the preparation of particles of controlled size and morphology including...
Scheme 1. Synthesis of PLLA_{36-b}-PDMAEMA_{216} and Removal of the RAFT End Group to Produce a Hydrogen-Terminated Polymer before Self-Assembly into Diamond-Shaped Platelets^4

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**RESULTS AND DISCUSSION**

**Synthesis of Diblock Copolymers.** On the basis of established synthetic methods, a PLLA macro-CTA was prepared by ring-opening polymerization (ROP) using a dual-functional initiator (Scheme 1).65,70 Reversible addition--fragmentation chain transfer (RAFT) polymerization was used to prepare a series of block copolymers with a poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) corona block with different block lengths (Table S1).1H NMR analysis confirmed the theoretical block ratios for each of the diblocks (Figure S1) over the core-to-corona ratio range of 1:1 to 1:9. A clear shift in molecular weight of the monomodal distributions with relatively narrow dispersities was confirmed by SEC refractive index (RI) analysis with good overlap of the UV (λ = 309 nm) trace, showing retention of the RAFT end group (Figure S2).
Self-Assembly of Diblock Copolymers. For the series of polymers with varying core-to-corona ratio, smooth diamond nanoplatelets were observed after 1 day of aging of a 5 mg mL⁻¹ ethanolic solution of diblock copolymer which had been heated for 4 h at 90 °C and then cooled to room temperature (Figure 1). Transmission electron microscopy (TEM) analysis revealed that platelets of uniform size (and hence surface area) were obtained from the self-nucleation of all of the PLLA-b-PDMAEMA block copolymers across the composition range investigated (Figure 1, Figure S3), where the zeta potential was measured as ca. +30 mV for all of the platelets formed (Table S2). Wide-angle X-ray scattering (WAXS) analysis was used to confirm the crystalline nature of the platelets, where a crystalline Bragg peak at 16.6° 2θ was observed, corresponding to the reflections of (110)/(200) planes in the crystalline domains of PLLA (Figure S4). On the basis of literature values, the unit cell of PLLA was reported to be orthorhombic with dimensions of \(a = 10.683 \pm 0.001 \text{ Å}, \ b = 6.170 \pm 0.001 \text{ Å}, \) and \(c = 28.860 \pm 0.004 \text{ Å}.\) In comparison to previous work, atomic force microscopy (AFM) also confirmed no significant difference in the thickness of the collapsed platelet (ca. 12 nm) between different core-to-corona block ratios (Figure S5). Indeed, liquid AFM analysis only suggested a minor difference of ca. 16 nm for the 1:6 ratio block copolymer versus ca. 20 nm for the 1:9 ratio block copolymer, accounting for the increased length of the corona chains (Figure S6).

According to scaling theory by Vilgis and Halperin, a polymer with longer corona chains is expected to form a thinner crystal with more chain-folds (to reduce unfavorable entropic penalties of the overlapping corona chains). In our system, no change in platelet thickness was observed (by dry state AFM measurements) across the series, and static light scattering (SLS) measurements suggested that platelets of the same size and thickness made by blocks of differing core-to-corona ratios have similar aggregation numbers (Figure S7). We hypothesize that the surplus spacing of the corona chain is such that the onset of tethered chain overcrowding has not yet been reached within the range of corona lengths used in this work (Figure 1f). Thus, there is no entropic penalty when increasing the corona block length, and no change in crystal thickness is required.

Notably, these well-defined platelets have been prepared with impressive uniformity without the need for seeded growth methods, which often require carefully controlled concentrations and aging processes. From this result, it is clear that the higher solubility of the PDMAEMA unimers, compared to our previous work primarily using a PDMA coronal block, did not allow for modulation of the number of seeds and hence alteration of the platelet’s size. Thus, we deduced that a more significant difference in solubility during the assembly process was required to achieve size control.

Size Control of Diamond Platelets. We then investigated the effect of changing solvent composition for the PLLA₃₆-b-PDMAEMA₂₁₆ diblock copolymer (1:6 core-to-corona ratio) in order to alter the unimer solubility during the crystallization process. On heating at 90 °C in ethanol, the addition of increasing amounts of tetrahydrofuran (THF) led to an exponential increase in the size of the diamond platelets, regardless of measurement by length or by area (Figure 2,

**Figure 1.** TEM micrographs of (a) PLLA₃₆-b-PDMAEMA₃₁₅, (b) PLLA₃₆-b-PDMAEMA₃₁₆, (c) PLLA₃₆-b-PDMAEMA₇₅, and (d) PLLA₃₆-b-PDMAEMA₅₅ diamond platelets. (e) Jitter box plot and average height data showing the negligible difference in area (as determined by TEM) and height of diamond platelets (as determined by AFM) regardless of block ratio. Samples were self-assembled at 90 °C for 4 h, cooled to room temperature, and aged for 1 day. Samples were stained with uranyl acetate. Scale bar = 1 μm. (f) Schematic of a crystallized PLLA-b-PDMAEMA polymer chain within a diamond-shaped platelet, showing a representation of the chain-folded core block and the spacing of the corona chain.
The difference in size was attributed to increased solubility producing fewer crystalline nuclei, thus leaving more unimers to grow along the crystal front. Furthermore, on increasing the heating time, no change in the size of the platelets was observed, indicating that the assemblies formed are indeed not simply kinetic products, but colloidally stable structures (Figure S9).

AFM analysis showed a consistent height of 12.3 ± 1.7 nm for all of the platelets prepared, typical of a polymer crystal with a single layer of chain folds (Figures 2 and S10). In this work, diamond-shaped platelets of up to ca. 3.75 μm in length were studied in detail; however, it should be noted that the addition of larger amounts of THF (14%) during the assembly process can be used to prepare even larger structures (ca. 9.5 μm in length, Figure S11). Significantly, freeze-dried platelets of all sizes, after removal of ethanol/THF, could be redispersed in water (at concentrations up to 50 mg mL−1) with no observed difference in their size or dispersity. Thus, these platelets in aqueous media were then considered as stabilizers in water-in-water emulsions.

**Pickering Emulsions.** Given the ability to control the surface area of the PLLA36-b-PDMAEMA216 platelets while maintaining the same chemical composition and the same thickness, we investigated their ability to act as Pickering emulsifiers. Indeed, previous research has indicated that clay and cellulose particles of different shapes have greater potential in stabilizing water-in-water emulsions.27−29 Herein, we precisely control the size of platelets with the same 2D shape to fully understand their potential to act as a stabilizer.

We used a 5 wt % dextran and 4 wt % PEG mixture as a model system, as this is well-known to phase separate into two macroscopically distinct layers consisting of a dextran-rich phase and a PEG-rich phase, as shown in previously reported phase diagrams,81 giving an ultralow interfacial tension of ca. 3.05 μN/m.22 These so-called rich phases, as opposed to pure dextran and pure PEG phases, can be partially accounted for by
the inherent high dispersity of the naturally occurring dextran and PEG polymers used; for example, smaller molecular weight dextran polymers are compatible in the PEG phase. Regardless, the water-in-water nature of this system is appropriately stable for the hydrophilic nature of the polymer corona chains present on both sides of the nanoplatelets, where the platelets show no significant preference for the PEG phase or the dextran phase by dynamic light scattering (DLS) measurements (Table S3). Evidence for a PEG in dextran emulsion (where the volume fraction of the dispersed phase is \( \varphi = 0.400 \)) was illustrated using fluorescence microscopy images of emulsions prepared using 0.01% of dextran labeled with fluorescein dye (Figure 3a).

It should be noted that a difference in droplet size was observed when using fluorescein-labeled dextran, where all droplet sizes appeared to marginally increase; however, this can be accounted for by the difference in molecular weight exhibited by SEC analysis (Figure S12). Hence, all subsequent measured droplet sizes without the use of fluorescein-labeled dextran are reported here.

To study the effect of platelet size on emulsion stability, the use of small diamond-shaped platelets (ca. 1.2 \( \times 10^3 \) nm\(^2\), prepared using 0% THF) and large diamond-shaped platelets (ca. 3.7 \( \times 10^3 \) nm\(^2\), prepared using 12% THF) were compared at different concentrations (0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 wt %). At a platelet content of up to 0.3 wt %, emulsions prepared with the small platelets were found to be unstable, whereas the droplets exhibited a loss of spherical shape with time and increased in size dramatically, with no droplets observed after 20 min. However, emulsions prepared with large platelets at a loading of 0.3 wt % showed a continuously consistent droplet size measured up to 60 min (Figures 3, S13 and S14), with eventual phase separation occurring after ca. 2 days. In a control experiment, emulsions prepared using PLLA\(_{156}\)-b-PDMAEMA\(_{216}\) spherical micelles (136 \( \pm 35 \) nm diameter, 5.4 \( \times 10^4 \) nm\(^2\) surface area, Figure S15) also showed a similar lack of stability to that of the small platelets, where the emulsion droplets again increased in size dramatically with phase separation observed after ca. 20 min (Figure S16). Conceptually, it is noteworthy that platelets of greater surface area provide improved stabilization, whereas platelets with a lower surface area, although possessing the same 2D shape, provide a similar lack of stabilization to that of their spherical counterparts.

We can attribute the increased stability to several factors. First, we consider that colloidal particles stabilize the emulsion by lowering the free energy. Given a uniform surface chemistry, the adsorption energy can be given by the following equation:

\[
\text{adsorption energy} \propto \frac{1}{\gamma}
\]

where \( \gamma \) is the interfacial tension and \( \sigma \) is the cross-sectional area of a colloidal particle.\(^{3,8,42} \) Given that the water-water interface has an ultralow interfacial tension, as previously discussed, the adsorption energy is relatively weak unless \( \sigma \) is sufficiently large enough to prevent coalescence of the droplets by keeping each water phase sufficiently apart. The use of large platelets allows for much larger \( \sigma \) value, thus reducing the free energy of adsorption, without increasing the mass of the particle such that sedimentation of the platelets and subsequent destabilization of the emulsion occur.\(^{29} \) The larger platelets also provide a greater barrier toward rotation, thus providing a more stable emulsion.\(^{39} \) Using a droplet relaxation method,\(^{81,83} \) the emulsion using large platelets also showed a drop in interfacial tension in comparison to the small platelet emulsion, indicating that surface area, and not simply a 2D shape, plays a key role in determining interfacial properties (Table S4, Figures S17 and S18). It should be noted that, previously, small Gibbsite (clay) platelets at similar loading levels were shown to produce more stable emulsions than larger platelets.\(^{29} \) However, in this case, the large Gibbsite platelets were also of increased thickness (30–40 nm vs. 7 nm), and therefore increased mass, which may account for the resulting destabilization.

Beyond 0.3 wt % of large platelets, the droplet size continued to remain consistent over time, and an increase in concentration only served to reduce the droplet size further, yet the surface coverage of the droplets did not exhibit any significant change (Figure 3e). Notably, the calculated coverage shows that even partial coverage of the emulsion colloids provide good stabilization, in accordance with previous work.\(^{28} \)

Further attempts to increase the stability using small platelets were also considered, namely, by significantly increasing the loading to 1 wt %, where an even greater total surface area is available to stabilize the emulsion droplets, resulting in a greater than maximum calculated coverage. However, this was also unsuccessful, where no decrease in droplet size was observed despite the high loading of the platelets (Figure S19). This emphasizes the importance of platelet size as opposed to platelet concentration, where a greater total surface area of the small platelets fails to achieve the same stabilization of the emulsion droplets as a lower total surface area of larger platelets. A similar platelet size effect was also observed using a 10 wt % dextran and 2 wt % PEG formulation (Figure S20), where the emulsion was found to be much less stable using small platelets, but exhibited a similar stability with the larger platelets, demonstrating that the small platelets continue to show lower efficiency even with a smaller dispersed phase (\( \varphi = 0.200 \)).

**Effect of Changing the Coronal Chemistry.** In order to investigate the stabilization of the emulsions further, we sought to monitor the effect of surface chemistry of the platelets. Using the 1:6 core-to-corona ratio block copolymer, modifications were carried out to prepare the equivalent sized platelets with quaternized and zwitterionic chemistries (Scheme 1, as confirmed by \(^1\)H NMR analysis and zeta potential measurements, Figures S21 and S22, Table S2). To ensure that the modified corona had no effect on the crystallization of the platelet, both modifications on the small and large platelets (prepared with 0% and 12% THF, respectively) were carried out after assembly, where TEM imaging revealed no noticeable difference in the dimensions of the platelets before and after modification (Figure S23).

At 0.3 wt %, both modifications resulted in lower emulsion stability in comparison to the unmodified platelets; however, the large platelet emulsions still continued to exhibit higher stability and smaller droplet sizes than the corresponding small platelet emulsions (Figure S24), thus further demonstrating that the platelet size (regardless of chemistry) plays a key role in emulsion stability. Noticeably, at 0.5 wt %, the emulsions using quaternized large platelets resulted in a much larger droplet size with phase separation observed after ca. 10 min, whereas the emulsions using zwitterionic large platelets resulted in a comparatively smaller droplet size with phase separation observed after ca. 35 min, though, again, both emulsions were still found to be less stable in comparison to the unmodified platelets (Figure S25). Though a drop in the interfacial tension was observed with the large zwitterionic platelets (Table, S4,
Figure S26), the short-term life of the corresponding small platelet emulsion and quaternized platelets did not allow measurement of the interfacial tension using the droplet relaxation method. Indeed, the overall lack of stabilization can be explained by the preference shown by the quaternized and zwitterionic platelets for the dextran phase, as measured by DLS analysis, where the larger structures observed in dextran solution account for the aggregation of the dextran molecules around the dispersed platelets in comparison to the smaller structures observed in PEG solution (Table S3). Indeed, on eventual phase separation, the neutral platelets appear to sit in the PEG-rich phase, whereas the quaternized and zwitterionic platelets sit in the dextran-rich phase (Figure S27).

Given that the more hydrophilic quaternized and zwitterionic platelets preferred the dextran-rich phase, we then investigated the effect of polymer hydrophilicity by removing the RAFT end group to produce a hydrogen-terminated polymer (Scheme 1) with the same corona chemistry as our most effective stabilizer. Using the 1:6 core-to-corona ratio block copolymer, a loss of the UV signal (λ = 309 nm) in SEC measurements confirmed that the end group had been sufficiently removed (Figure S28). A solvent composition of 12% THF in ethanol was used as to prepare large diamond platelets as discussed previously. However, the size of the platelets increased (ca. 5.5 × 10^6 nm², Figure S29a), likely as a result of the increased unimer solubility (in removing a small hydrophobic group) leading to improved crystallization. In order to monitor the effect of the coronal chemistry only, the assembly conditions were modified to prepare platelets of a similar size to those discussed previously as “large” platelets. As such, it was found that 10% THF allowed the preparation of diamond-platelets of comparable size (ca. 4.0 × 10^6 nm², Figure S29b). Using a 5 wt % dextran and 4 wt % PEG mixture with 0.5 wt % of these platelets to prepare the emulsion, a similar decrease in Pickering stabilization was observed, where the droplet size increased to eventual phase separation after ca. 10 min (Figure S30). Consistent with the zwitterionic and quaternized platelet emulsions, the phase separated emulsion showed the end group removed platelets were present in the dextran-rich phase (Figure S31), thus explaining the overall lack of long-term stabilization with such chemistries. However, regardless of the duration of stabilization, it is especially noteworthy that the size of the platelet plays a key role in its ability to act as an emulsifier, where the use of a larger platelet results in improved stabilization for all of the surface chemistries studied.

CONCLUSIONS

We have successfully demonstrated the formation of uniform 2D diamond-shaped nanoplatelets with a range of different sizes (up to ca. 9.5 μm in length) using biorelevant poly(lactide) block copolymers. We have achieved significant control over their surface area while maintaining a single crystal thickness. Importantly, this can be achieved without modifying the chemistry of the copolymer or its block ratios, but instead using a simple unimer solubility approach, where the addition of “good” solvents can be used to achieve greater unimer solubility and hence allow for the preparation of larger and more perfect single crystal assemblies. This unprecedented control over surface area was exploited in the design of Pickering water-in-water emulsifiers, where we have shown that larger platelets (ca. 3.7 × 10^6 nm²) attain smaller droplet sizes and more stable emulsions than smaller platelets (ca. 1.2 × 10^5 nm²) at concentrations as low as 0.3 wt %. We propose that this is due to their large surface area which exhibits greater adsorption properties, and a larger barrier towards rotation of the particles. Though it is noted that stable emulsions can only be prepared when the particles show little preference for either phase, the platelet size-emulsion stability trend was observed across a range of coronal chemistries. This highlights that the ability to control the size of 2D platelets can allow for the design of effective interfacial stabilizers for application in water-in-water emulsions. Such 2D platelets of controlled dimensions and chemistries are expected to find further utilization in the pharmaceutical, agrochemical, green chemistry, cosmetics, and/or food industry.

ASSOCIATED CONTENT

Supporting Information

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PLL A, poly(l-lactide); CDSA, crystallization-driven self-assembly; ROP, ring-opening polymerization; RAFT, reversible addition–fragmentation chain-transfer polymerization; PDMAEMA, poly(dimethylaminoethyl methacrylate); THF, tetrahydrofuran; TEM, transmission electron microscopy; AFM, atomic force microscopy; PEG, poly(ethylene glycol); DLS, dynamic light scattering; WAXS, wide-angle X-ray scattering; PRINT, particle replication in nonwetting template; SLS, static light scattering

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