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Pickering Emulsifiers Based on Block Copolymer Nanoparticles Prepared by Polymerization-Induced Self-Assembly

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ABSTRACT. Block copolymer nanoparticles prepared *via* polymerisation-induced self-assembly (PISA) represent an emerging class of organic Pickering emulsifiers. Such nanoparticles are readily prepared by chain-extending a soluble homopolymer precursor using a carefully selected second monomer that forms an insoluble block in the chosen solvent. As the second block grows, it undergoes phase separation that drives *in situ* self-assembly to form sterically-stabilized nanoparticles. Conducting such PISA syntheses in aqueous solution leads to *hydrophilic* nanoparticles that enables the formation of oil-in-water emulsions. Alternatively, *hydrophobic* nanoparticles can be prepared in non-polar media (e.g. *n*-alkanes) which enables water-in-oil emulsions to be produced. In this review, the specific advantages of using PISA to prepare such bespoke Pickering emulsifiers are highlighted, which include fine control over particle size, morphology and surface wettability. This has enabled various fundamental scientific questions regarding Pickering emulsions to be addressed. Moreover, block copolymer nanoparticles can be used to prepare Pickering emulsions over various length scales, with mean droplet diameters ranging from millimeters to less than 200 nm.

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INTRODUCTION

At the turn of the last century, Ramsden[1] and Pickering[2] independently discovered that various types of particles can stabilize emulsions. Over the past two decades, seminal studies by Binks and co-workers have led to a resurgence of interest in such Pickering emulsions.[3-8] This is because particulate emulsifiers offer numerous advantages over conventional surfactant or polymeric emulsifiers, including superior long-term emulsion stability and reduced foaming during homogenization.[6] Consequently, Pickering emulsions have been evaluated for various applications in food manufacture,[9-11] agrochemicals,[12-15] cosmetics[16-17] and pharmaceuticals.[17-20]

It is well-known that surfactants typically adsorb and desorb from interfaces on rapid timescales.[21] Unlike surfactants, colloidal particles that adsorb at oil/water or air/water interfaces are not necessarily amphiphilic.[3, 5-7, 22-23] Nevertheless, particles are often irreversibly adsorbed at an interface if they are of sufficient size and have appropriate surface wettability.[24-26] The driving force for particle adsorption is minimization of the interfacial area, which lowers the free energy of the system.[6, 21] The amount of energy, ΔE, required to remove a spherical particle of radius r from the oil/water interface is given by equation 1:[27]

$$\Delta E = \pi r^2 \gamma_{\mathrm{ow}} (1 \pm \cos\theta_w)^2 \quad (1)$$

where γ_{ow} is the oil/water interfacial tension and θ_{w} is the three-phase contact angle. Figure 1 shows how the three-phase contact angle affects the detachment energy for a 20 nm particle adsorbed at the toluene/water interface.[5] The calculated energy of detachment is greatest for $\theta_{\mathrm{w}} = 90°$ and falls rapidly either side of this value. The contact angle is directly related to the particle wettability, which dictates the type of emulsion that is formed.[6] More specifically, *hydrophilic* particles are preferentially wetted by the aqueous phase ($\theta_{\mathrm{w}} < 90°$) and hence form oil-in-water (o/w) emulsions. In contrast, *hydrophobic* particles ($\theta_{\mathrm{w}} > 90°$) give rise to water-in-oil (w/o) emulsions.[5] In principle, using a judicious combination of hydrophilic and hydrophobic particles should enable the preparation of either water-in-oil-in-water (w/o/w) or oil-in-water-in-oil (o/w/o) Pickering double emulsions.[28-29]

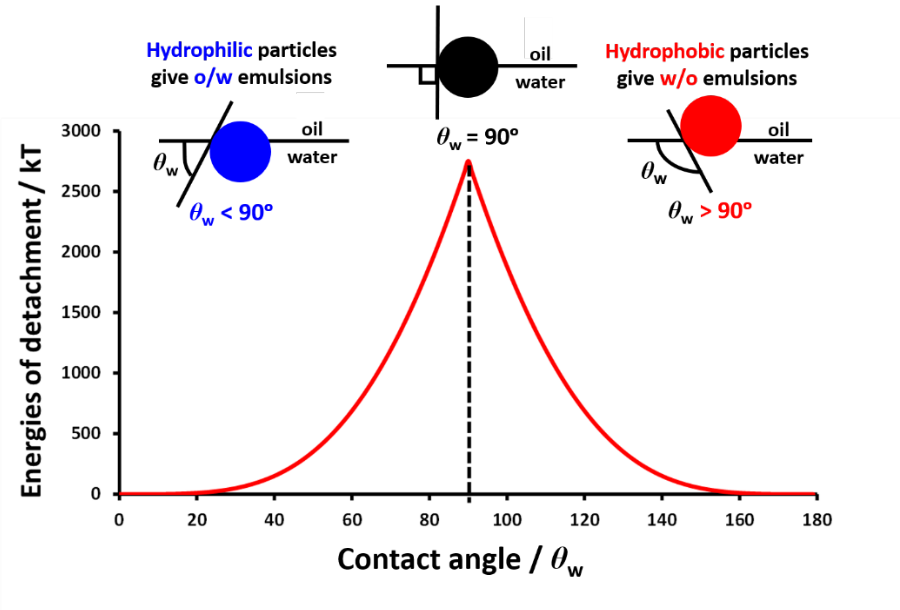

Figure 1. Spatial location of a spherical particle adsorbed at a planar oil-water interface for a contact angle θ_w measured through the aqueous phase such that θ_w is less than 90° (blue), equal to 90° (black) or greater than 90° (red). In general, hydrophilic particles ($\theta_w < 90°$) form oil-in-water (w/o) Pickering emulsions, whereas hydrophobic particles ($\theta_w > 90°$) give rise to water-in-oil (w/o) Pickering emulsions. The energy of detachment versus contact angle is shown for the specific case of a spherical nanoparticle of 10 nm radius adsorbed at a planar toluene-water interface for which $\gamma_{ow} = 0.036$ Nm^{-1}.[5-6]

Many types of inorganic particles have been utilized as Pickering emulsifiers, including silica,[3, 30] titania,[31-32] magnetite,[33] and clay.[3-4, 30-31, 33-37] Similarly, various organic particles such as cellulose nanorods,[38-41] carbon black,[42-43] carbon nanotubes,[44] graphene oxide sheets[45-46] and aqueous polymer particles (e.g. latexes,[22, 47-54] microgels[55-56] and block copolymer nanoparticles[57]) have been evaluated in this context. Within the latter category, it is typically found that charge-stabilized latexes produce w/o emulsions whereas sterically-stabilized latexes usually form o/w emulsions, as depicted in Figure 2.[22, 49] Based on seminal studies by Binks and others, the use of *inorganic* particles to form Pickering emulsions is well understood.[6, 21, 26, 35, 58-65] In the prototypical case of silica, particle wettability can be tuned by partial alkylation of the silanol surface groups[5] or by adding either a cationic surfactant[61, 66] or electrolyte.[3, 34] However, such approaches tend to produce incipient flocculation in solution, which in turn leads to the formation of relatively thick multilayers of adsorbed particles. In principle, polymer-based particles offer several advantages as Pickering emulsifiers. If they are designed to have appropriate surface wettability, no surface modification is required and adsorption at the oil-water interface leads to the formation of well-defined monolayers.[3, 8, 22, 51, 57, 67-74] Moreover, surface wettability can be readily tuned by selecting an appropriate steric stabilizer block[73]

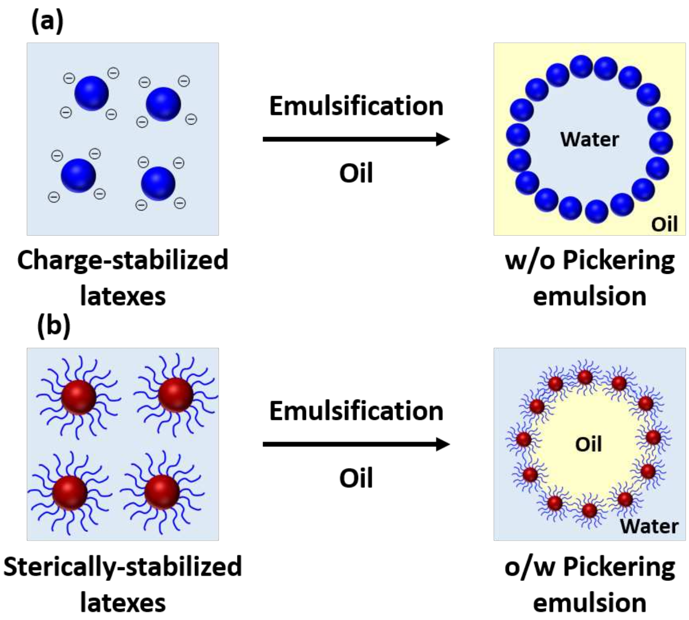

Figure 2. Schematic representation of the formation of (a) water-in-oil (w/o) Pickering emulsions using charge-stabilized latex particles or (b) oil-in-water (o/w) Pickering emulsions using sterically-stabilised latex particles via high-shear homogenization of an aqueous dispersion of latex particles with oil.

Velev and co-workers were the first to report using latex particles as Pickering emulsifiers.[47] In this case, the oil phase was 1-octanol and charge-stabilized polystyrene particles bearing either sulfate or amidine surface groups were utilized. Subsequently, Binks et al. used near-monodisperse polystyrene latex particles to stabilize w/o Pickering emulsions using cyclohexane as a model oil.[22] Weitz and co-workers developed colloidosomes using water-in-decalin Pickering emulsions stabilized by 0.7 μm poly(methyl methacrylate) latex particles coated in a layer of poly(hydroxystearic acid).[48]

Subsequently, Binks, Armes and co-workers prepared a pH-sensitive polystyrene latex using a poly[2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate] (PDMA-

PMMA) diblock copolymer as a steric stabilizer. The cationic character of the PDMA block could be adjusted by controlling the solution pH.[49] Such latex particles adsorbed onto *n*-hexadecane droplets when high shear homogenization was conducted at pH 8 to produce stable Pickering emulsions. However, stable emulsions could not be obtained at pH 3 because protonation of the PDMA block led to highly hydrophilic particles that were insufficiently wetted by the oil phase. Thus, such latexes simply exhibit pH-*dependent* Pickering emulsifier behavior,[75] as opposed to the pH-*responsive* behavior that was originally (and erroneously) reported.[49-50] In a related study, the thermoresponsive nature of the same PDMA-PMMA-stabilized polystyrene latex particles was explored.[51] Heating an o/w emulsion stabilized by such particles up to 70 °C (i.e. above the cloud point of the hydrophilic PDMA block) led to significant droplet coalescence. Moreover, w/o emulsions were obtained if the same aqueous latex and oil were separately heated to 70 °C prior to emulsification. The relatively hydrophobic nature of the flocculated particles under such conditions accounts for this phase inversion.[51]

In related work, Fujii et al. prepared lightly cross-linked poly(4-vinylpyridine)/silica nanocomposite particles for use as *stimulus-responsive* Pickering emulsifiers.[76-77] Such particles stabilized Pickering emulsions at pH 8-9, but addition of acid caused rapid demulsification. This is because protonation of the 4-vinylpyridine units at low pH induces particle swelling: lateral repulsion between the resulting highly swollen cationic microgel-like particles leads to their desorption from the oil-water interface. Similarly, pH-responsive Pickering emulsifiers based on polymer latexes also been reported. For example, Morse and co-workers prepared lightly cross-linked latexes composed of either poly(2-(*tert*-butylamino)ethyl methacrylate) or poly(2-(diethylamino)ethyl methacrylate).[78-79] Such sterically-stabilized latexes act as effective Pickering emulsifiers at pH 10 but acidification resulted in rapid demulsification owing to a latex-to-microgel transition. In principle, such

Pickering emulsifiers can be reused by raising the solution pH to its original value. In practice, the progressive build-up of background salt leads to a gradual reduction in microgel swelling, which effectively limits the number of pH cycles.[79]

Another class of stimulus-responsive Pickering emulsifier is the poly(*N*-isopropylacrylamide) (PNIPAM)-based microgels originally reported by Ngai et al. and further developed by Richtering and co-workers.[55-56, 80-81] PNIPAM homopolymer exhibits a lower critical solution temperature (LCST) at around 32 °C.[82] Thus, aqueous dispersion copolymerization of NIPAM with bisacrylamide cross-linker using persulfate as a free radical initiator at 70 °C affords a charge-stabilized latex and the resulting lightly cross-linked particles exhibit a latex-to-microgel transition on cooling below this temperature.[83-85] Moreover, pH-responsive PNIPAM-based microgels can be prepared by introducing methacrylic acid (MAA) as a comonomer. Ngai et al. reported the first example of a dual temperature- and pH-responsive Pickering emulsifier.[55, 80] The incorporation of MAA units within the PNIPAM-based particles led to microgel swelling on raising the solution pH. Thus, o/w emulsions stabilized by such P(NIPAM-*co*-MAA) microgels are stable at 25 °C and pH 9.4, but become unstable at 60 °C on lowering the pH to 6.1.[55, 80] This is because the adsorbed microgels shrink at the oil-water interface, thus leading to a reduction in surface coverage and hence droplet coalescence.[86] In follow-up studies, Richtering and co-workers have postulated that the viscoelastic behavior of the microgel-coated interface determines the emulsion stability.[56, 81, 87-90]

The invention of living anionic polymerization by Szwarc et al.[91-92] in the 1950s ultimately enabled the rational design of various examples of amphiphilic diblock copolymers such as poly(ethylene oxide)-polystyrene or poly(acrylic acid)-polystyrene. It is well-established by Eisenberg et al.[93-95] and others[96] that such amphiphilic diblock copolymers undergo self-assembly in aqueous solution to form spherical, worm-like or vesicular nano-objects.[93-94, 96-98] Such self-assembly is enthalpically driven and depends on both χ and N, where χ is the Flory-Huggins interaction parameter and N is the overall degree of polymerization of the copolymer chains.[97] However, traditional post-polymerization processing routes invariably involve organic co-solvents such as DMF or THF, gradual addition of water over prolonged time scales and relatively low copolymer concentrations (< 1.0% w/w), which unfortunately preclude many potential commercial applications.

Fortunately, the development of controlled radical polymerization techniques[99-101] such as reversible addition-fragmentation chain transfer (RAFT) polymerization[102-105] has enabled the efficient synthesis of block copolymer nano-objects *via* polymerization-induced self-assembly (PISA).[106-115] Importantly, RAFT polymerization is exceptionally tolerant of monomer functionality, which enables the rational design of nano-objects bearing hydroxyl, amine or carboxylic acid groups. Moreover, such PISA syntheses can be conducted at relatively high copolymer concentrations (up to 50% w/w).[116-117] In a typical protocol, a soluble homopolymer is chain-extended using a second monomer in a suitable solvent such that the growing second block gradually becomes insoluble, which drives *in situ* self-assembly to form diblock copolymer nanoparticles, as depicted in Figure 3. Depending on the solubility of the second monomer in the continuous phase, the synthesis of the insoluble second block involves either dispersion or emulsion polymerization.[108, 118-134] Systematic variation of the relative volume fractions of the two blocks provides control over the copolymer morphology.[116, 135-136] Over the past decade or so, the generic nature of PISA has been demonstrated for a wide range of vinyl monomers in various solvents including water,[132, 137-143] polar solvents (e.g. ethanol or methanol),[144-157] non-polar solvents (e.g. *n*-alkanes),[110, 158-163] ionic liquids,[164] silicone oil[165-166] and supercritical CO_2.[167-170] Typically, pseudo-phase diagrams are constructed to enable the reproducible targeting of morphologies for a given PISA formulation.[140] The basic design rules for the preparation of spheres,[140, 158] worms,[171-175] vesicles,[176-179] framboidal vesicles,[72, 137, 180-181] and lamellae[182-184] are now well-established. In many cases, the final copolymer morphology is dictated primarily by the relative volume fractions of the two blocks, as indicated by the geometric packing parameter introduced by Israelachvili and co-workers to account for surfactant self-assembly.[185] For example, spheres are produced when using a relatively long soluble stabilizer block and/or working at relatively low copolymer concentrations,[140, 158] while vesicles can be obtained when targeting highly asymmetric diblock compositions (i.e. relatively long insoluble blocks) at higher copolymer concentrations.[137, 145] It is also well-established that worm-like particles typically occupy relatively narrow phase space between that of spheres and vesicles,[162, 171-172] framboidal vesicles can be produced from ABC triblock copolymers in which the B and C blocks are both insoluble and enthalpically incompatible,[72, 186] and targeting stiff, inflexible insoluble blocks favors lamellae formation.[183-184]

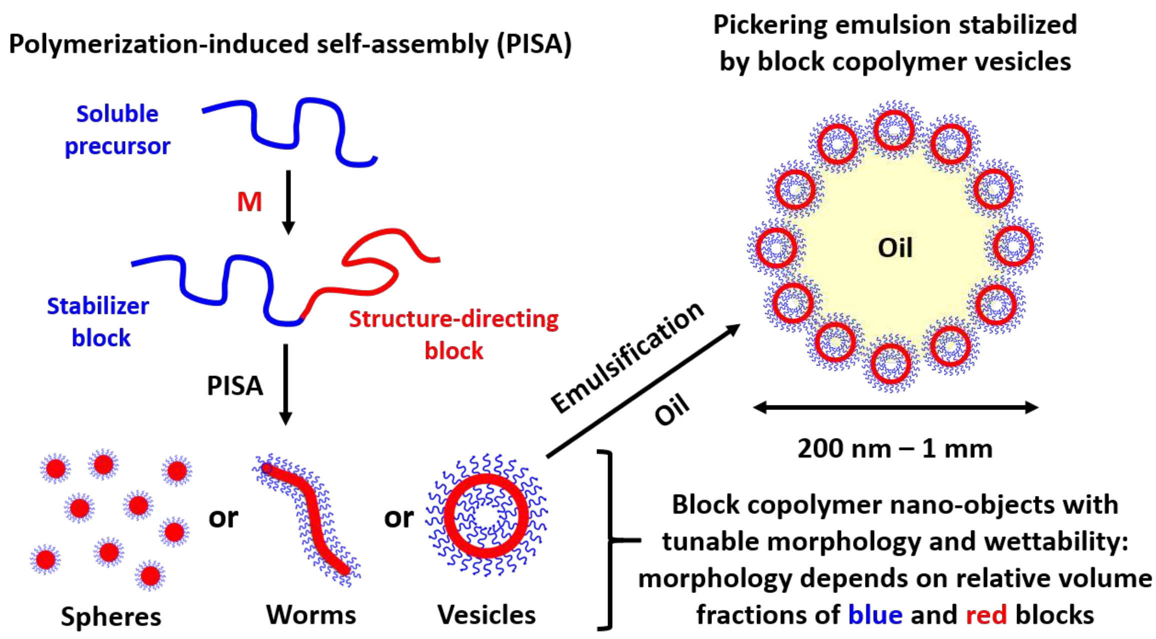

Figure 3. Schematic representation of polymerization-induced self-assembly (PISA), whereby a soluble blue precursor block is chain-extended using a suitable vinyl monomer to produce a red insoluble structure-directing block. Depending on the relative volume fractions of the blue and red blocks, *in situ* self-assembly produces either spheres, worms or vesicles. PISA can be conducted in either water or various oils. In the case of aqueous PISA, addition of a suitable oil followed by emulsification via high shear homogenization leads to the formation of Pickering emulsions, as illustrated above for the case of vesicles.[187]

Recently, we have exploited PISA to design new block copolymer nano-objects for use as bespoke Pickering emulsifiers.[71-74, 117, 187-195] More specifically, PISA enables the copolymer morphology and surface chemistry to be tuned by judicious selection of the soluble stabilizer and insoluble structure-directing blocks. Such syntheses can be conducted in either water or in *n*-alkanes to afford either *hydrophilic* or *hydrophobic* sterically-stabilized nanoparticles, respectively. Such nanoparticles can be used to prepare oil-in-water,[117, 187-188] water-in-oil[71, 189] and multiple emulsions.[73, 191] In particular, the versatility offered by PISA enables interesting scientific questions to be addressed in the context of Pickering emulsions. Do such linear block copolymer nanoparticles survive high-shear homogenization or is their covalent stabilization required? Can we readily distinguish between these two scenarios? Can vesicles be used to stabilize Pickering emulsions? Do worms offer any advantages over spheres? Does refractive index matching enable highly transparent Pickering emulsions to be prepared? Can spheres be made sufficiently small (and stable) to enable the preparation of Pickering nanoemulsions? What is the effect of introducing minimal nanoparticle surface charge on Pickering emulsion formation and stability? Such research topics are discussed in the remaining sections of this review article.

EFFECT OF COPOLYMER MORPHOLOGY ON PICKERING EMULSIFIER PERFORMANCE

Thompson et al. reported the first example of polymer-based Pickering emulsifiers prepared via PISA.[187] Linear poly(glycerol monomethacrylate)-poly(2-hydroxypropyl methacrylate) $PGMA_{45}$-$PHPMA_{200}$ diblock copolymer vesicles were prepared at 10% w/w solids using a RAFT aqueous dispersion polymerization formulation (see Figure 4a). Such linear (non-cross-linked) vesicles did not survive the high-shear homogenization conditions required for emulsification with *n*-dodecane. Instead, *in situ* dissociation occurred and the resulting oil droplets became stabilized by individual amphiphilic $PGMA_{45}$-$PHPMA_{200}$

chains. This problem was confirmed using two characterization techniques. Firstly, the volume-average oil droplet diameter determined by laser diffraction proved to be independent of the copolymer concentration (see Figure 4b), whereas a strong concentration dependence is invariably observed for Pickering emulsions.[58, 196]

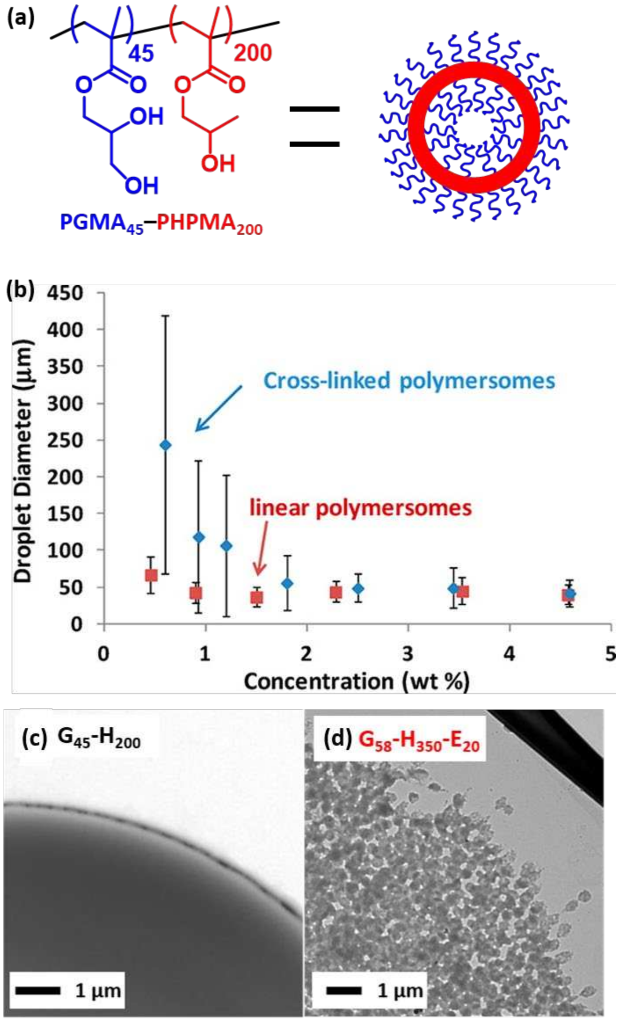

Figure 4. (a) Chemical structure of linear PGMA45-PHPMA200 vesicles. (b) Volume-average droplet diameter (obtained by laser diffraction) vs. copolymer concentration for both linear PGMA45-PHPMA200 and cross-linked PGMA58-PHPMA350-PEGDMA20 vesicles. TEM images recorded for an individual dried cross-linked colloidosome prepared using (c) linear PGMA45-PHPMA200 vesicles and (d) cross-linked PGMA58-PHPMA350-PEGDMA20 vesicles. Reproduced from ref. 187 (Copyright 2012 American Chemical Society).

Secondly, TEM studies of the dried oil droplets indicated a smooth, featureless morphology with no evidence for the original vesicles, see Figure 4c.This study highlighted the importance of verifying the formation of genuine Pickering emulsions when using block copolymer nanoparticles. *In situ* vesicle dissociation was attributed to the weakly hydrophobic nature of the membrane-forming PHPMA block.[197-198] In view of this problem, ethylene glycol dimethacrylate (EGDMA) was added as a third comonomer to form cross-linked vesicles, which proved to be stable when subjected to high-shear homogenization.[187] In this case, the expected upturn in oil droplet diameter was observed as the vesicle concentration was lowered. Furthermore, TEM studies revealed the presence of intact vesicles at the oil/water interface (see Figure 4c). Such vesicle-stabilized Pickering emulsions could be covalently-stabilized by dissolving a tolylene-2,4-diisocyanate-terminated poly(propylene glycol) diisocyanate cross-linker (PPG-TDI) in the oil phase prior to homogenization, leading to the formation of so-called colloidosomes.[48, 187, 199]

Turbidimetry experiments indicated that most of the vesicles were not adsorbed at the oil/water interface and instead remained within the continuous aqueous phase. As the copolymer concentration used to prepare such Pickering emulsions was reduced from 2.5% to 0.6% w/w, the vesicle adsorption efficiency increased from 57 to 78% w/w. The relatively weak affinity of the vesicles for the oil/water interface is presumably related to their aqueous cores, which necessarily lowers the Hamaker constant and hence reduces the enthalpy of adsorption.

Subsequently, Thompson and co-workers reported that linear PGMA-PHPMA spheres and worms also underwent *in situ* dissociation to form soluble copolymer chains during high shear homogenization.[188] However, laser diffraction studies confirmed that this problem could be circumvented by either covalent stabilization using EGDMA cross-linker or by addition of a sufficiently hydrophobic third block such as poly(benzyl methacrylate) (PBzMA), see Figure 5. Using the former strategy, $PGMA_{100}$–$PHPMA_{200}$–$PEGDMA_{20}$ spheres and $PGMA_{45}$–$PHPMA_{100}$–$PEGDMA_{10}$ worms were prepared via PISA and their performance as putative Pickering emulsifiers for the stabilization of *n*-dodecane-in-water emulsions was compared.[188] It is well-established that worms are formed during PISA via 1D stochastic fusion of multiple spheres.[139-140, 200] This is important, because it means that the mean worm thickness is directly related to the dimensions of the initial spheres. Moreover, given that both types of nanoparticles utilized a hydroxyl-functional PGMA block as a steric stabilizer (see Figure 4a), essentially identical surface wettabilities can be assumed. Thompson and co-workers[188] argued that, for sufficiently anisotropic worms, their specific surface area, A_w, can be estimated using the relation $A_w \sim 2/\rho R$, where ρ is the particle density and R is the mean worm cross-sectional radius. In contrast, prior to their 1D fusion to form worms, the spheres have a specific surface area, A_s, given by $A_s = 3/\rho r$, where r is the mean sphere radius and, to a reasonable approximation, $r \sim R$. Therefore, the reduction in specific surface area (A_w/A_s) that occurs during the 1D fusion of multiple spheres to form a single worm is only around 33%, whereas the energy of attachment of a sufficiently anisotropic worm ($L/2R > 20$) composed of x spheres is estimated to be at least x times higher than the individual spherical nanoparticles. In summary, highly anisotropic diblock copolymer worms are expected to adsorb at an oil-water interface much more strongly than the corresponding precursor diblock copolymer spheres, while retaining a relatively high specific surface area. Turbidimetry studies conducted on the lower aqueous phase formed after emulsion creaming indicated relatively high adsorption efficiencies (~90%) for both spheres and worms. More importantly, the worms produced significantly finer *n*-dodecane droplets than the spheres. This was attributed to the highly anisotropic nature of the former nanoparticles, which allows the droplet surface to become sufficiently coated to prevent coalescence at approximately half the surface coverage. Similar observations were made by Vermant and co-workers, who found that Pickering emulsions prepared using polystyrene rods were more stable relative to their spherical precursors.[201-202] Such experiments account for the excellent Pickering emulsion performance observed for highly anisotropic cellulose nanofibers, for which no spherical counterparts exist.[38] More broadly, various groups have reported that model anisotropic particles differ fundamentally in their interfacial adsorption behavior compared to isotropic particles.[54, 203-205]

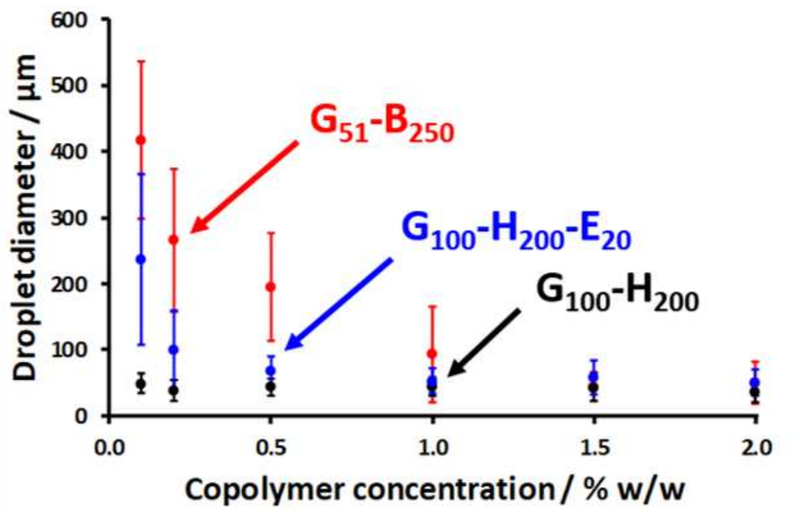

Figure 5. Volume-average droplet diameter versus copolymer concentration obtained by laser diffraction analysis of *n*-dodecane-in-water emulsions prepared using linear (red) $PGMA_{51}$-$PBzMA_{250}$, (black) $PGMA_{100}$–$PHPMA_{200}$ spheres and (blue) cross-linked $PGMA_{100}$–$PHPMA_{200}$–$PEGDMA_{20}$ spheres. Error bars represent the standard deviation for each droplet diameter, rather than the experimental error. Reproduced from ref. 188 (Copyright 2014 Royal Society of Chemistry).

Thompson et al. also directly compared the Pickering emulsifier performance of linear hydrophobic poly(lauryl methacrylate)−poly(benzyl methacrylate) (PLMA−PBzMA) worms and spheres prepared in *n*-dodecane.[189] For this PISA formulation, the worms are thermoresponsive and can be transformed into spheres when heated to 150 °C owing to surface plasticization of the core-forming PBzMA chains.[159] Moreover, this morphological transition is effectively irreversible if it is conducted at sufficiently low copolymer concentration (e.g., ≤ 1.0% w/w).[159] Thus, the Pickering performance of highly anisotropic $PLMA_{16}$−$PBzMA_{37}$ worms for the stabilization of w/o emulsions could be compared to that of *chemically identical* spheres for the first time. Again, significantly smaller mean droplet diameters *(D*) were observed for the worms when working above a certain critical copolymer mass (m_p). Furthermore, the fractional droplet surface coverage, *C*, differed markedly for worms and spheres (see Figure 6). As expected, spherical nanoparticles exhibited a constant surface coverage with copolymer concentration. In contrast, higher surface coverages were observed for worms at higher copolymer concentration. The isotropic nature of spheres means that maximum packing requires six inter-particle contacts with nearest neighbors, whereas worms can form a loose packing at low concentration and a more densely-packed layer at relatively high concentration. Similar observations have been made for anisotropic cellulose nanofibers.[38-39] Relatively short fibers formed a densely-packed layer at the oil/water interface, whereas longer fibers led to lower surface coverages with a more open 2D network.[39] Small-angle X-ray scattering (SAXS) studies conducted on a worm-stabilized Pickering emulsion indicated that the mean thickness of the worm layer surrounding the water droplets is comparable to the worm cross-sectional diameter. This indicates monolayer coverage rather than multilayer formation. Finally, the thermoresponsive behavior of $PLMA_{16}$–$PBzMA_{37}$ worms was exploited to induce demulsification. Heating the w/o Pickering emulsion up to 95 °C induces a worm-to-sphere transition, with concomitant droplet coalescence being observed owing to copolymer desorption from the oil/water interface.

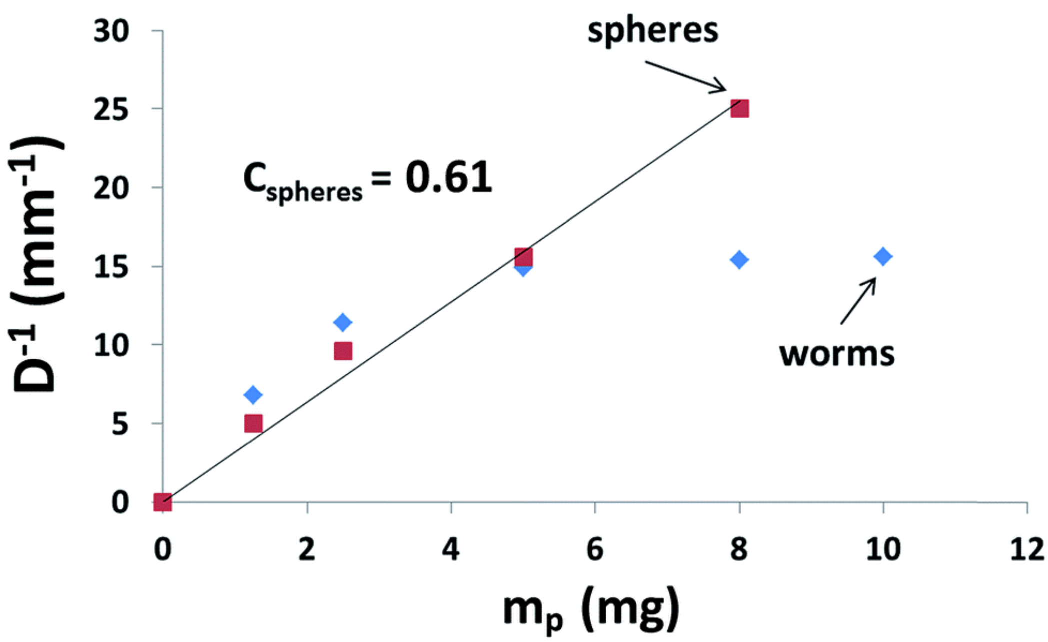

Figure 6. Effect of varying the copolymer particle mass m_p on the mean droplet diameter D for two series of water-in-*n*-dodecane emulsions stabilized using $PLMA_{16}$-$PBzMA_{37}$ spheres (red circles) and $PLMA_{16}$-$PBzMA_{37}$ worms (blue squares). Note the deviation from linearity for the latter particles. Reproduced from ref. 189 (Copyright 2015 Royal Society of Chemistry).

Xue and co-workers compared the stability of diblock copolymer worms and spheres when such nano-objects were subjected to high-shear homogenization.[206] To prepare such diblock copolymer nanoparticles, poly(*N*-(2-methacryloyloxy)ethyl pyrrolidone) ($PNMP_{53}$) was chain-extended by RAFT polymerization of 2-perfluorooctylethyl methacrylate (FMA) in chloroform. The resulting $PNMP_{53}$-$PFMA_x$ block copolymers were then self-assembled to form either spheres (x = 5) or worms (x = 10) in water by traditional post-polymerization processing via a solvent switch. Oil-in-water Pickering emulsions were prepared by high shear homogenization of aqueous dispersions of such nanoparticles with *n*-dodecane. TEM and laser diffraction studies confirmed that both types of nanoparticles survived emulsification, presumably owing to the highly hydrophobic nature of the PFMA core-forming block. This study used the twisted intramolecular charge transfer state (TICT) of Nile Red to distinguish between the fluorescence of this dye dissolved in *n*-dodecane droplets and that within the nanoparticle cores. More specifically, the excitation and emission wavelengths for Nile Red dissolved in *n*-dodecane are 490-520 nm and 530-570 nm respectively, whereas these bands are red-shifted to 576 nm and 621 nm respectively for the dye-loaded nanoparticles.[206] Thus, if Nile Red was solubilized within the nanoparticles prior to emulsification, excitation at 576 nm led to significantly greater fluorescence intensity than that observed for the oil droplets, indicating that the nanoparticles were adsorbed at the oil/water interface in the form of Pickering emulsions.

The effect of varying the shear rate on the fluorescence intensity of the dye dissolved in the oil droplets (I_{oil}) relative to that for the dye-loaded $PNMP_{53}$-$PFMA_5$ spheres (I_{layer}) was also examined. As expected, greater shear rates led to higher I_{oil}/I_{layer} ratios (see Figure 7).[206] For example, dye fluorescence originating from the oil droplets dominates at 24,000 rpm, indicating that such conditions cause *in situ* nanoparticle dissociation, leading to emulsion stabilization by the individual amphiphilic $PNMP_{53}$-$PFMA_5$ diblock copolymer chains. A similar experiment was conducted using the $PNMP_{53}$-$PFMA_{10}$ worms. In this case, at least some of the worms remained intact at 24,000 rpm. The authors of this study attributed this observation to the worms being less susceptible to degradation under shear than the spheres. However, it seems much more likely that the greater stability of the worms is simply the result of the higher DP of the hydrophobic PFMA block that is required to form such nano-objects.[188] Although these $PNMP_{53}$-$PFMA_x$ spheres and worms were prepared by traditional post-polymerization processing, this study is clearly consistent with the observation of *in situ* nanoparticle dissociation reported when using linear diblock copolymer nano-objects prepared via PISA. Moreover, it confirms that such dissociation can occur even when using highly hydrophobic perfluorinated structure-directing blocks, although the mean DPs of such chains are admittedly rather low.

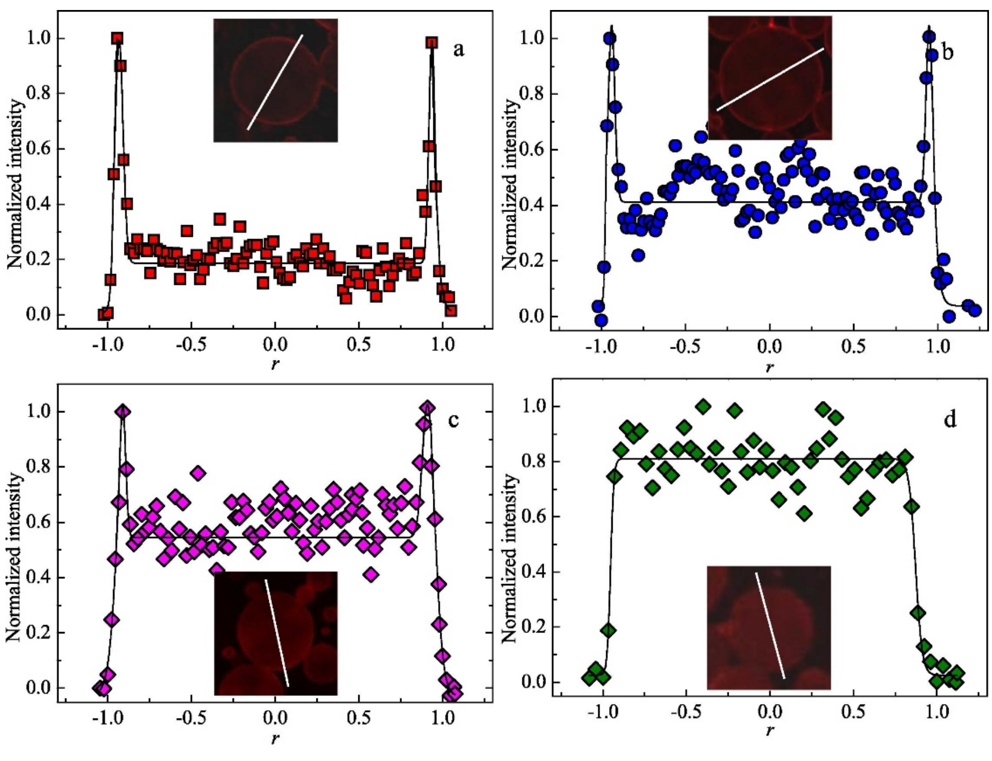

Figure 7. Fluorescence data recorded as a function of distance *r* (with data fits using both Gaussian and Boltzmann methods) obtained for an *n*-dodecane-in-water Pickering emulsion prepared at an oil volume fraction of 0.50 using 0.50% w/w $PNMP_{53}$-$PFMA_5$ via high shear homogenization at (a) 6,000 rpm, (b) 12,000 rpm, (c) 18,000 rpm or (d) 24,000 rpm, respectively. In each case, the inset confocal microscopy image shows the individual emulsion droplet and the white line indicates the cross-sectional diameter through which the fluorescence intensity is calculated as a function of *r*. Reproduced from ref. 206 (Copyright 2020 Elsevier).

Recently, we reported the effect of nanoparticle anisotropy on the stability of an o/w Pickering emulsion in the presence of a non-ionic surfactant.[194] RAFT aqueous dispersion polymerization was used to prepare epoxy-functional $PGMA_{48}$-P($HPMA_{90}$-*stat*-$GlyMA_{15}$) worms (where GlyMA denotes glycidyl methacrylate). The thermoresponsive nature of such linear precursor nanoparticles was exploited to produce either relatively long or relatively short cross-linked worms of essentially the same copolymer composition.[207] More specifically, 3-aminopropyltriethoxysilane (APTES) was utilized in a post-polymerization crosslinking protocol developed by Lovett et al.[208] The primary amine group in this reagent reacts with the epoxy groups on the GlyMA units while its siloxy groups react with the secondary alcohol groups on the HPMA units to confer covalent stabilization. Either relatively long or relatively short cross-linked worms were prepared to stabilize *n*-dodecane-in-water Pickering emulsions, with a fluorescent label being introduced by reacting rhodamine B piperazine with a minor fraction of the epoxy groups on the GlyMA residues prior to APTES addition. This enabled fluorescence microscopy to be used to monitor the precise location of the worms before and after addition of the non-ionic surfactant to each Pickering emulsion (see Figure 8). A much higher surfactant concentration was required to displace long worms from the oil/water interface compared to the short worms. This is because the former nanoparticles are much more strongly adsorbed than the latter.[188-189]

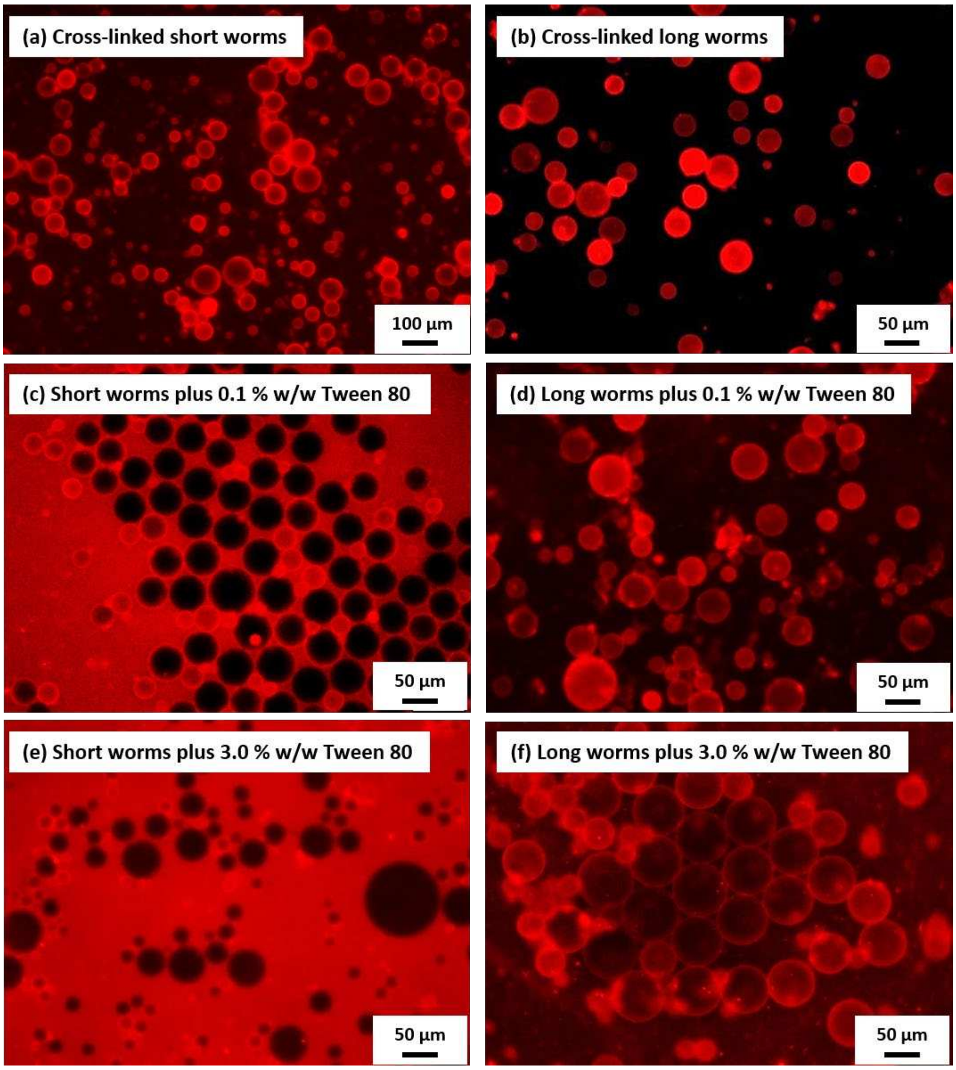

Figure 8. Fluorescence microscopy images obtained for emulsions prepared by high shear homogenization of 0.25% w/w aqueous $PGMA_{48}$-P($HPMA_{90}$-*stat*-$GlyMA_{15}$) copolymer dispersions with 50 vol % *n*-dodecane at 13,500 rpm for 2 min, before and after addition of either 0.1% or 3.0% w/w non-ionic surfactant (Tween 80). (a) Pickering emulsion stabilized using short $PGMA_{48}$-P($HPMA_{90}$-*stat*-$GlyMA_{15}$) cross-linked worms (b) Pickering emulsion stabilized using long $PGMA_{48}$-P($HPMA_{90}$-*stat*-$GlyMA_{15}$) cross-linked worms. (c) Surfactant-stabilized emulsion obtained after addition of 0.1% w/w Tween 80, which displaces the short worms initially adsorbed at the oil/water interface. (d) Pickering emulsion obtained after addition of 0.1% w/w Tween 80, which *cannot* displace the long worms initially adsorbed at the oil/water interface. (e) Surfactant-stabilized emulsion obtained after addition of 3.0% w/w Tween 80, which displaces the short worms adsorbed at the oil/water interface. (f) Mixed emulsion obtained after addition of 3.0% w/w Tween 80, which *partially* displaces the long worms adsorbed at the oil/water interface. Reproduced from ref. 194 (Copyright 2018 American Chemical Society).

Zhang and co-workers utilized cross-linked triblock copolymer worms to prepare high internal phase Pickering emulsions (HIPEs) in which the volume fraction of the dispersed phase exceeded 0.74.[209] Such worms were first prepared *via* RAFT dispersion polymerization of BzMA in ethanol using a poly(2-(dimethylamino)ethyl methacrylate) (PDMA) precursor. These linear $PDMA_{37}$-$PBzMA_{96}$ worms were subsequently cross-linked via chain extension using EGDMA. After transferring the covalently-stabilized $PDMA_{37}$-$PBzMA_{96}$-$PEGDMA_{9}$

worms into water, the resulting dispersion was subjected to high shear homogenization with varying amounts of cyclohexane. Highly viscous HIPEs possessing an internal phase ranging from 0.77 to 0.84 exhibited good long-term stability. Furthermore, a remarkably low copolymer concentration (0.3%) was sufficient to stabilize a HIPE prepared at an oil volume fraction of 0.77. This remarkable observation was attributed to the dense gel network formed by the highly anisotropic worms. To prepare porous monoliths, either silica or Fe_3O_4 nanoparticles were added to the aqueous phase prior to homogenization to act as a co-stabilizer. After freeze-drying for 12 h, the 3D hierarchical structure survived in the form of a free-standing porous monolith. In the case of the Fe_3O_4 nanoparticles, such ultralight hybrid materials proved to be responsive to an applied magnetic field.[209]

Chambon and co-workers reported that chain extension of PGMA-PHPMA precursor vesicles using a water-immiscible monomer such as BzMA or MMA resulted in the formation of framboidal (raspberry-like) triblock copolymer vesicles *via* seeded RAFT aqueous emulsion polymerization.[186] Subsequently, a series of $PGMA_{63}$-$PHPMA_{350}$-$PBzMA_z$ framboidal vesicles were evaluated by Mable et al. as putative Pickering emulsifiers.[72] As expected, the $PGMA_{63}$-$PHPMA_{350}$ precursor vesicles did not survive the high shear conditions required to generate Pickering emulsions. In contrast, $PGMA_{63}$-$PHPMA_{350}$-$PBzMA_z$ vesicles led to the formation of genuine Pickering emulsions, as confirmed by laser diffraction and TEM studies.[72] Moreover, the strongly hydrophobic nature of the third PBzMA block proved to be sufficient to prevent vesicle dissociation. Turbidimetric analysis of the lower aqueous phase after emulsion creaming was again used to assess the Pickering emulsifier performance of these framboidal vesicles. Systematic variation of the DP (z) of the PBzMA block enabled their surface roughness to be tuned, which enabled the adsorption efficiency to be determined as a function of surface roughness (see Figure 9c) Increasing the PBzMA DP (z) from 25 to 125 at a constant copolymer concentration led to an increase in adsorption efficiency from 36% to 94%. Furthermore, framboidal vesicles with optimal surface roughness exhibited significantly higher adsorption efficiency than that observed for non-framboidal $PGMA_{63}$-$PHPMA_{350}$-$PEGDMA_{20}$ cross-linked vesicles (67%).[187]

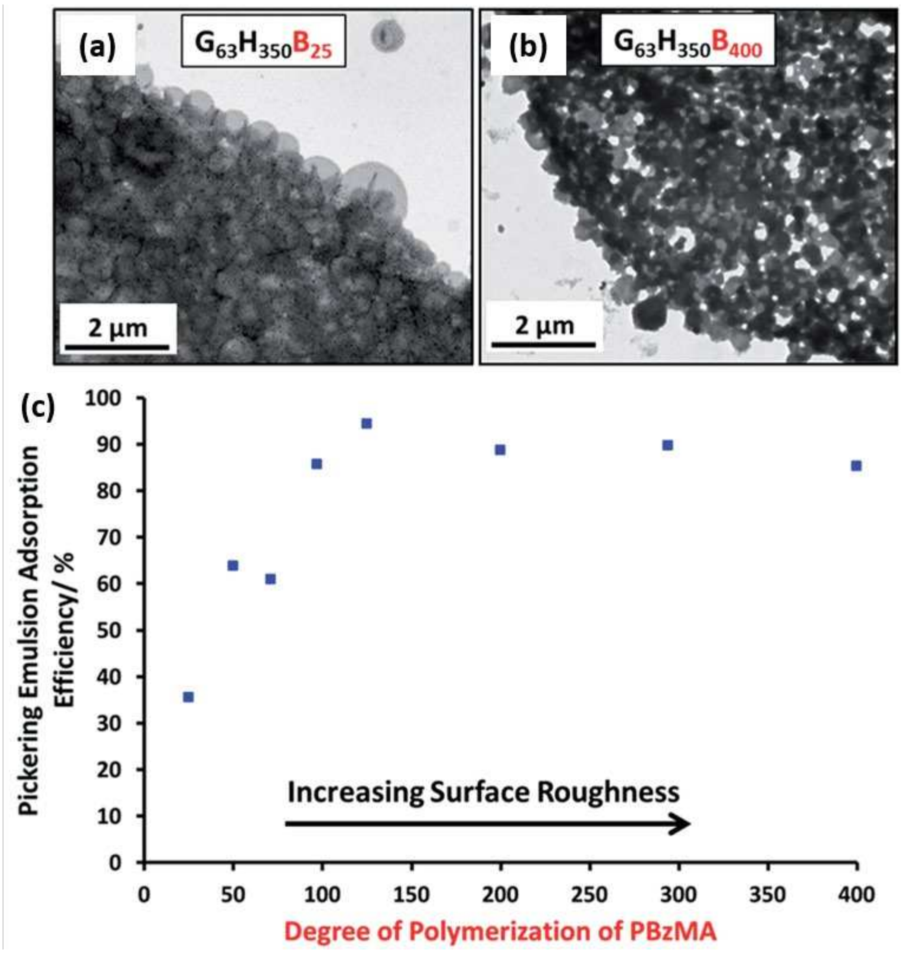

Figure 9. TEM images obtained for Pickering emulsions of *n*-dodecane stabilized using aqueous dispersions of (a) $PGMA_{63}$-$PHPMA_{350}$-$PBzMA_{25}$ and (b) $PGMA_{63}$-$PHPMA_{350}$-$PBzMA_{400}$ vesicles. (c) Variation of Pickering emulsion adsorption efficiency (A_{eff}) against PBzMA DP for a series of $PGMA_{63}$-$PHPMA_{350}$-PBzMA vesicles of increasing surface roughness. Reproduced from ref. 72 (Copyright 2015 Royal Society of Chemistry).

Another example of framboidal vesicles was reported by Xiu and co-workers.[181] In this case, PGMA-PHPMA precursor vesicles were chain-extended using GlyMA *via* seeded RAFT aqueous emulsion polymerization, resulting in the formation of epoxy-functional framboidal vesicles. Such framboidal vesicles were shown to be an efficient Pickering emulsifier for *n*-hexane-in-water emulsions, with higher PGlyMA DPs and copolymer concentrations leading to the formation of finer oil droplets.

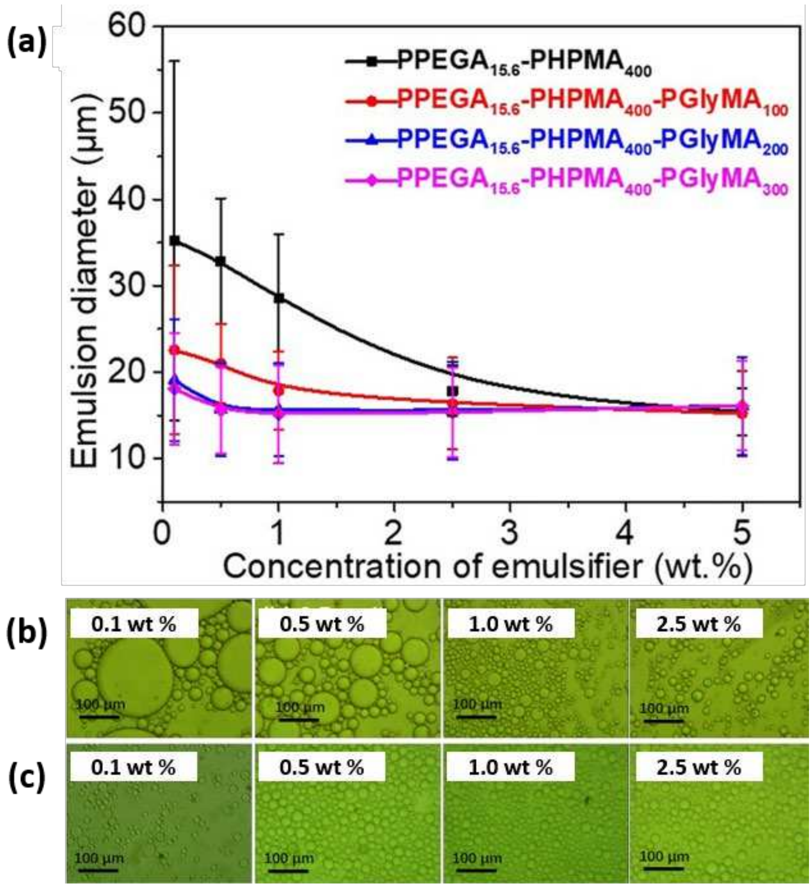

Figure 10. (a) Effect of varying the copolymer concentration on the mean droplet diameter of Pickering emulsions prepared using $PPEGA_{15.6}$–$PHPMA_{400}$–$PGlyMA_n$ multicompartment block copolymer nanoparticles (MBCPs). Optical microscopy images recorded for *n*-hexane-in-water emulsions stabilized using (b) $PPEGA_{15.6}$–$PHPMA_{400}$ precursor nanoparticles and (c) epoxy-functionalized $PPEGA_{15.6}$–$PHPMA_{400}$–$PGlyMA_{300}$ nanoparticles at the stated copolymer concentrations. Reproduced from ref. 210 (Copyright 2019 American Chemical Society).

The same research group also evaluated so-called multicompartment block copolymer nanoparticles (MBCPs) as Pickering emulsifiers.[210] Such nanoparticles were prepared *via* photoinitiated PISA in a two-step synthesis. First, a poly(poly(ethylene glycol) methyl ether acrylate) (PPEGA) precursor was chain-extended via RAFT aqueous dispersion polymerization of HPMA to yield well-defined spheres. Such spheres were then chain-extended using GlyMA to produce MBCP nanoparticles. The Pickering performance of the precursor $PPEGA_{15.6}$-$PHPMA_{400}$ spheres was compared to that of the final $PPEGA_{15.6}$-$PHPMA_{400}$-$PGlyMA_n$ particles, which had a distinctly framboidal morphology. There was an upturn in the mean droplet diameter at lower copolymer concentrations, indicating the formation of genuine Pickering emulsions (see Figure 10). As previously discussed, PHPMA-core diblock copolymer nanoparticles typically dissociate to form individual copolymer chains during high shear homogenization.[72, 187-188, 194] In contrast, laser diffraction data suggested that the $PPEGA_{15.6}$-$PHPMA_{400}$ precursor nanoparticles survive emulsification intact.[211] Increasing the DP of the PGlyMA block up to 300 led to greater surface roughness, lower limiting copolymer concentrations and the formation of finer emulsion droplets for a given copolymer concentration.

A summary of the majority of the block copolymer nano-objects discussed in this section and their Pickering emulsifier performance is shown in Table 1.

Table 1. Summary of Pickering emulsions prepared using block copolymer nanoparticles of differing morphologies.

block copolymer composition	copolymer morphology	Linear or cross-linked?	emulsion type	Genuine Pickering emulsion?	Ref.
$PGMA_{45}$-$PHPMA_{200}$	vesicular	linear	o/w	no	187
$PGMA_{58}$-$PHPMA_{350}$-$PEGDMA_{20}$	vesicular	cross-linked	o/w	yes	187
$PGMA_{63}$-$PHPMA_{350}$-$PBzMA_{25}$	vesicular	linear	o/w	yes	72
$PPEGA_{15.6}$–$PHPMA_{400}$–$PGlyMA_{300}$	multicompartmental	linear	o/w	yes	210
$PGMA_{100}$-$PHPMA_{200}$-$PEGDMA_{20}$	spherical	cross-linked	o/w	yes	188
$PGMA_{45}$-$PHPMA_{140}$	worm-like	linear	o/w	no	188
$PGMA_{45}$-$PHPMA_{100}$-$PEGDMA_{10}$	worm-like	cross-linked	o/w	yes	188
$PGMA_{51}$-$PBzMA_{50}$	spherical	linear	o/w	yes	188
$PGMA_{37}$-$PHPMA_{60}$-$PBzMA_{30}$	worm-like	linear	o/w	yes	188
$PNMP_{53}$-$PFMA_{5}$	spherical	linear	o/w	Depends on shear-rate	206
$PNMP_{53}$-$PFMA_{10}$	worm-like	linear	o/w	yes	206
$PGMA_{48}$-P($HPMA_{90}$-stat-$GlyMA_{15}$)	short worms	cross-linked	o/w	yes	194
$PGMA_{48}$-P($HPMA_{90}$-stat-$GlyMA_{15}$)	long worms	cross-linked	o/w	yes	194
$PLMA_{16}$–$PBzMA_{37}$	worm-like	linear	w/o	yes	189
$PLMA_{16}$–$PBzMA_{37}$	spherical	linear	w/o	yes	189

DESIGN OF PICKERING EMULSIFIERS WITH TUNABLE SURFACE WETTABILITY

Using either hydrophilic or hydrophobic stabilizer blocks enables PISA to be conducted in either polar or non-polar solvents. As already noted, the chemical nature of the stabilizer block directly influences the surface wettability of such block copolymer nanoparticles and therefore dictates the type of Pickering emulsion that is formed. For example, PGMA-stabilized spheres, worms or vesicles invariably stabilize oil-in-water emulsions.[72-73, 117, 187, 191] Clearly, the hydrophilic PGMA chains produce a three-phase particle contact angle of less than 90°. In contrast, the core-forming block has little or no influence over surface wettability of such particles, with o/w Pickering emulsions being obtained when using either weakly hydrophobic (cross-linked) PHPMA cores[187-188] or strongly hydrophobic cores such as PBzMA.[117] On the other hand, using a highly hydrophobic stabilizer block such as PLMA or poly(stearyl methacrylate) (PSMA) almost invariably leads to the formation of w/o Pickering emulsions.[73-74, 189, 212] Such nanoparticles are preferentially wetted by the oil to produce a three-phase contact angle of more than 90°.

Thompson et al. used hydrophobic $PLMA_{16}$-$PBzMA_{37}$ worms in conjunction with hydrophilic $PGMA_{37}$-$PHPMA_{60}$-$PBzMA_{30}$ worms to prepare Pickering double emulsions.[73] Figure 11 shows how either water-in-oil-in-water (w/o/w) or oil-in-water-in-oil (o/w/o) Pickering double emulsions could be obtained depending on the emulsification protocol. The former emulsions were obtained by first preparing a precursor w/o emulsion stabilized using $PLMA_{16}$-$PBzMA_{37}$ worms. A relatively high stirring rate of 24,000 rpm was chosen to generate the smallest possible mean droplet diameter. Subsequently, this w/o emulsion was then homogenized with an equal volume of an aqueous dispersion of $PGMA_{37}$-$PHPMA_{60}$-$PBzMA_{30}$ worms. A lower stirring rate of 7,000 rpm was used in this step to produce larger aqueous droplets and hence favor formation of the desired w/o/w Pickering double emulsion.

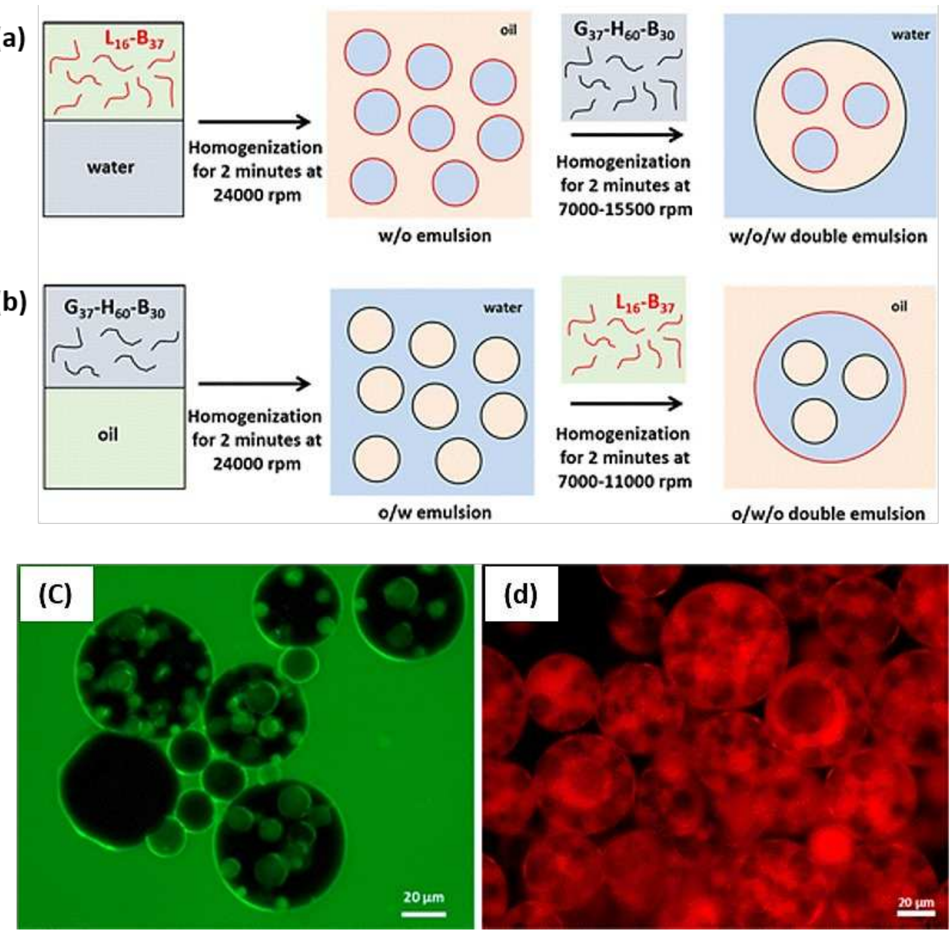

Figure 11. Schematic representation of the preparation of (a) w/o/w double emulsions and (b) o/w/o double emulsions by the judicious combination of the two types of highly anisotropic block copolymer worms as Pickering emulsifiers. Fluorescence microscopy images confirm the successful formation of w/o/w Pickering double emulsions where (c) the aqueous phase is labeled with fluorescein and (d) the *n*-dodecane phase is labeled with Nile Red. Reproduced from ref. 73 (Copyright 2015 American Chemical Society).

Similarly, o/w/o Pickering double emulsions could be prepared by first homogenizing a precursor o/w emulsion stabilized using $PGMA_{37}$-$PHPMA_{60}$-$PBzMA_{30}$ worms, followed by its homogenization with an equal volume of *n*-dodecane containing $PLMA_{16}$-$PBzMA_{37}$ worms.

More recently, Rymaruk and co-workers reported that a range of poly(3-[tris(trimethylsiloxy)silyl]propyl methacrylate)-poly(benzyl methacrylate) (PSiMA-PBzMA) spheres could be prepared directly in a low-viscosity silicone oil (DM5).[213] Such sterically-stabilized nanoparticles were evaluated as Pickering emulsifiers for ten bio-sourced oils. For three of these oils, using a copolymer concentration of 2.0% w/w and a DM5 volume fraction of 0.50 led to the formation of oil-in-oil Pickering emulsions, with DM5 forming the continuous phase in each case (Figure 12a). Such emulsions remained stable for at least two months when stored at 20 °C. To improve the Pickering emulsifier performance of such PSiMA-stabilized spheres, lauryl methacrylate (LMA) was statistically copolymerized with BzMA when preparing the core-forming block. The resulting optimized $PSiMA_{19}$-$P(BzMA_{190}$-*stat*-$LMA_{10})$ nanoparticles enabled the formation of stable oil-in-oil emulsions when using nine of the ten bio-sourced oils, as shown in Figure 12b.

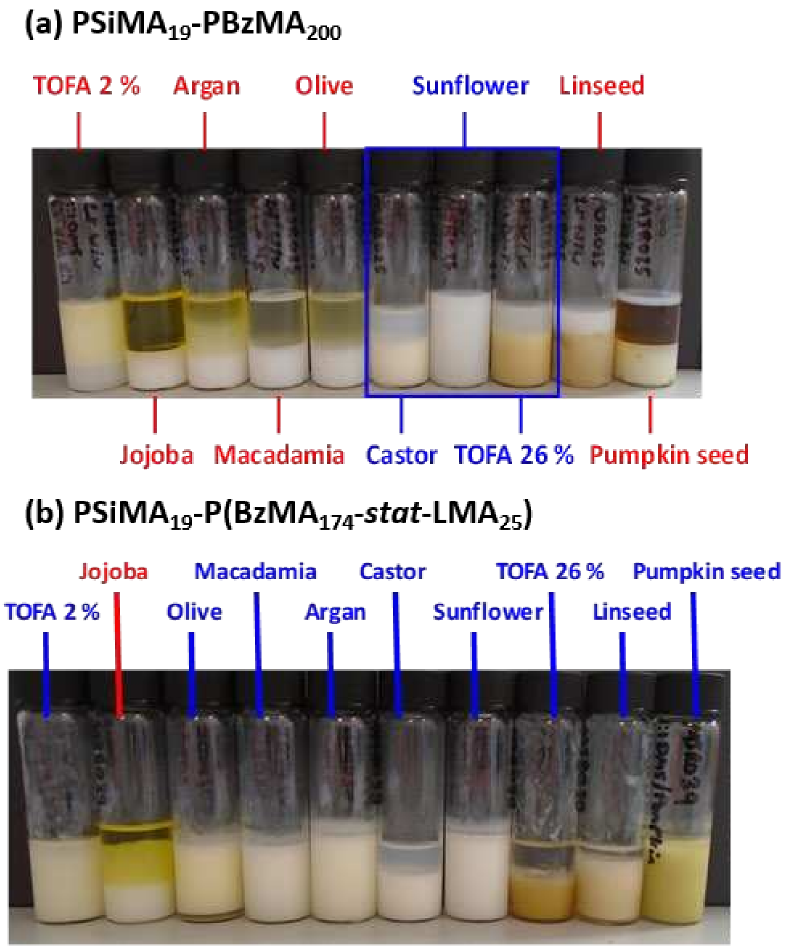

Figure 12. (a) Digital photograph recorded after standing for two months at 20 °C showing various bio-sourced oil-in-oil Pickering emulsions prepared using a 2.0% w/w dispersion of $PSiMA_{19}$-$PBzMA_{200}$ spheres in a silicone oil (DM5). Each bio-sourced oil is indicated above or below the relevant vial: emulsions that remained stable after two months are denoted in blue, whereas those that undergo (partial) phase separation on this time scale are shown in red. (b) Digital photograph of various oil-in-DM5 Pickering emulsions prepared using a 2.0% w/w dispersion of $PSiMA_{19}$-$P(BzMA_{174}$-*stat*-$LMA_{25})$ spheres in DM5 recorded after storage for two months at 20 °C. In each case, the DM5 volume fraction was 0.50 and the $PSiMA_{19}$-$P(BzMA_{175}$-*stat*-$LMA_{25})$ concentration was 2.0% w/w. Emulsions that remained stable after two months are indicated in blue, whereas the single jojoba oil-based emulsion that underwent phase separation over this time period is shown in red. Reproduced from ref. 213 (Copyright 2020 Elsevier).

This was attributed to enhanced wettability of the nanoparticles by the bio-sourced oil, thus leading to stronger interfacial adsorption. This study clearly demonstrates that the chemical nature of the *core-forming* block can influence the surface wettability of block copolymer nanoparticles, in addition to that of the *stabilizer* block.

An and co-workers prepared oil-in-oil HIPEs from semi-fluorinated block copolymer nanoparticles.[214] Spherical diblock copolymer nanoparticles were initially prepared in DMF *via* RAFT dispersion polymerization of heptadecafluorodecyl methacrylate (HDFDMA) using a $PMMA_{43}$ precursor. Such $PMMA_{43}$-$PHDFDMA_{50}$ nanoparticles were transferred into DMSO and subsequently subjected to high shear homogenization with cyclohexane (volume fraction = 0.80). This led to the formation of a highly viscous cyclohexane-in-DMSO HIPE. This is an example of non-aqueous HIPE which have rarely been reported.[215-216] In the same study, $PSMA_{15}$-$PHDFDMA_{50}$ short rods were prepared via RAFT dispersion polymerization in *n*-dodecane. A 5% w/w dispersion of such nanoparticles could be used to prepare relatively stable DMF-in-*n*-dodecane Pickering emulsion by homogenization with an equivalent volume of DMF. This is a rather rare example of such an emulsion, not least because these two solvents are usually considered to be miscible.[217]

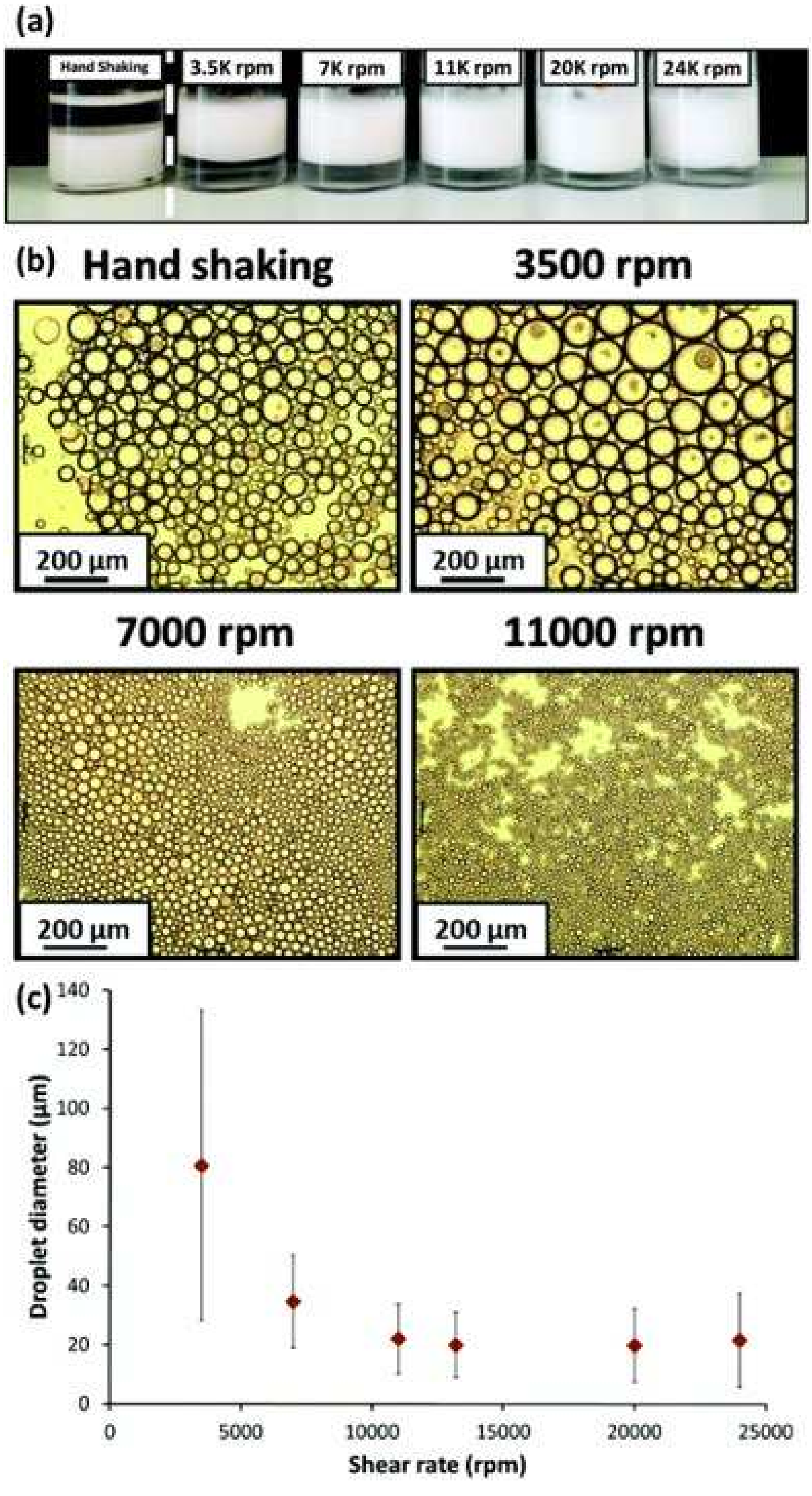

Figure 13. (a) Digital photographs obtained for the Pickering emulsions prepared using 1.0% w/w $PSMA_{14}$–$PNMEP_{49}$ spherical nanoparticles at various shear rates. Oil-in-water emulsions are formed in all cases, except when hand-shaking is used; this latter approach instead results in the formation of a water-in-oil emulsion. (b) Optical microscopy images recorded for the droplets prepared *via* hand-shaking, or *via* homogenization at 3,500 rpm, 7,000 rpm or 11,000 rpm (scale bar = 200 µm). (c) Shear rate dependence for the mean droplet diameter (as determined by laser diffraction) of Pickering emulsions prepared using $PSMA_{14}$–$PNMEP_{49}$ spheres as the sole emulsifier. The error bars represent the standard deviation of each volume-average droplet diameter, rather than the experimental error. Reproduced from ref. 212 (Copyright 2016 Royal Society of Chemistry).

In general, block copolymer nanoparticles comprising a hydrophilic stabilizer block are expected to produce o/w emulsions, while those prepared with a hydrophobic stabilizer block should afford w/o emulsions. However, block copolymer nanoparticles prepared by RAFT dispersion polymerization in non-polar oils comprising a relatively hydrophilic core-forming block do not appear to follow this general rule. For example, Cunningham and co-workers reported that poly(stearyl methacrylate)–poly(*N*-2-(methacryloyloxy)ethyl pyrrolidone) ($PSMA_{14}$–$PNMEP_{49}$) spheres prepared in *n*-dodecane could form either w/o or o/w Pickering emulsions depending on the emulsification conditions.[212] Thus, o/w emulsions were obtained when conducting high shear homogenization with an equal volume fraction of water at 3,500-24,000 rpm, whereas emulsification by hand-shaking led to w/o emulsions. This unexpected result was attributed to *in situ* inversion of the nanoparticles during homogenization to form hydrophilic $PNMEP_{49}$-$PSMA_{14}$ block copolymer spheres. As expected, increasing the shear rate led to a reduction in the main oil droplet diameter (see Figure 13c). Increasing the oil volume fraction from 50% v/v up to 75% v/v prevented nanoparticle inversion and hence enabled the formation of w/o Pickering emulsions.

In a related study by György et al., the Pickering emulsifier behavior of $PSMA_{12}$-$PHPMA_{50}$ spheres was explored.[218] In this case, the relatively polar PHPMA core-forming block is not actually water-soluble, hence different emulsifier behavior was anticipated. In this case, the emulsion type depended on the water volume fraction. At relatively low water volume fractions (0.125 – 0.375), w/o Pickering emulsions were obtained at 1.0% w/w copolymer concentration. However, using water volume fractions of 0.50 – 0.75 led to formation of a w/o/w Pickering double emulsion, as confirmed by fluorescence microscopy. Thus, this is a rare example of a double emulsion that can be prepared using a *single* copolymer composition.

STABILIZATION OF GIANT PICKERING DROPLETS

In recent years, there have been a number of reports of particle-stabilized droplets of the order of 1-2 mm diameter.[190, 195, 219-226] Such 'giant' Pickering emulsions are typically prepared using capillaries and can act as model systems to provide useful insights into coalescence behavior[221] and particle adsorption kinetics.[195] The use of spherical latex particles to stabilize 'giant' Pickering emulsions has been studied in some detail.[220] Thompson et al. used conventional free radical polymerization to prepare PGMA-stabilized polystyrene latexes of either 135 nm or 905 nm diameter *via* aqueous emulsion or alcoholic dispersion polymerization, respectively.[221] Such latexes were then used them to prepare millimeter-sized *n*-dodecane droplets. High speed video imaging was used to monitor the coalescence of these latex-coated droplets.[219] Longer coalescence times were observed for Pickering emulsions prepared using the 902 nm latex and either bilayer formation or a bridging monolayer occurred prior to coalescence.[221] Giant colloidosomes were produced by adding an oil-soluble cross-linker (PPG-TDI) to the oil phase (sunflower oil) prior to droplet formation.[221] Cross-linking for 20 min at 25 °C led to a reduction in the interfacial elasticity and prevented any droplet coalescence. In contrast, giant oil droplets coated with charge-stabilized poly(*tert*-butylamino)ethyl methacrylate (PTBAEMA) latex particles coalesced on close contact in the absence of any PPG-TDI cross-linker.[224]

Block copolymer nanoparticles prepared *via* PISA have also been used as emulsifiers for millimeter-sized droplets.[190, 195] As previously discussed, linear PGMA-PHPMA block copolymer worms are unstable with respect to nanoparticle dissociation when subjected to high shear homogenization. However, a highly hydrophobic block (e.g. PBzMA) can be added to the nanoparticle cores to confer stability. Thus, Mable et al. prepared linear PGMA-PHPMA-PBzMA triblock copolymer worms *via* RAFT-mediated PISA.[190] Such worms were evaluated as Pickering emulsifiers for the stabilization of o/w emulsions prepared under low shear conditions (i.e. hand-shaking). Optical microscopy and laser diffraction studies confirmed that the worms survived such emulsification conditions and adsorbed intact at the oil/water interface. Much larger millimeter-sized oil droplets were produced using hand-shaking compared to those using high shear homogenization. In contrast to the PGMA-PHPMA-PBzMA worms, droplet diameters for emulsions prepared using PGMA-PHPMA worms remained relatively constant with increasing copolymer concentration. This indicates that such worms dissociate even during low shear emulsification, generating individual amphiphilic diblock copolymer chains adsorbed at the oil/water interface, rather than nanoparticles.

Subsequently, Cunningham et al. used either 22 nm diameter $PGMA_{39}$-$PBzMA_{60}$ spheres or $PGMA_{37}$-$PHPMA_{60}$-$PBzMA_{30}$ worms (mean worm width = 26 nm) in turn to stabilize millimeter-sized *n*-dodecane droplets.[195] Dynamic interfacial tension measurements were conducted to assess the kinetics of adsorption for these two morphologies. In both cases, a rapid initial reduction in interfacial tension occurred within 20 s, with a more gradual but still significant reduction being observed thereafter. This provided direct evidence for nanoparticle adsorption at the oil/water interface and suggested the possibility of post-adsorption nanoparticle reorganization. The worms lowered the interfacial tension significantly more than the spheres, indicating that the former had a stronger affinity for the *n*-dodecane/water interface. Both spheres and worms stabilized 'giant' Pickering droplets but the former proved to be more effective at stabilizing the interface in the absence of any interfacial ageing. This was attributed to the very high capillary pressure generated by such small nanoparticles. In contrast, the significantly larger worms required interfacial ageing for at least 90 s before droplet stability was achieved owing to their slower diffusion to the interface and rearrangement after initial adsorption. Systematic variation of the copolymer concentration revealed that the worms were able to stabilize 'giant' Pickering emulsions at lower concentrations than the equivalent 22 nm spheres. Finally, the effect of mean sphere diameter on droplet coalescence time was examined for 22, 41, 60 and 91 nm $PGMA_{39}$-$PBzMA_x$ spheres (see Figure 14). Stable droplets were obtained using either 22 nm or 41 nm spheres, but coalescence was always observed when using 60 nm and 91 nm spheres, even after relatively long ageing times. Presumably, this reduction in droplet stability is related to the lower capillary pressure for such larger particles, since all other parameters remained constant.

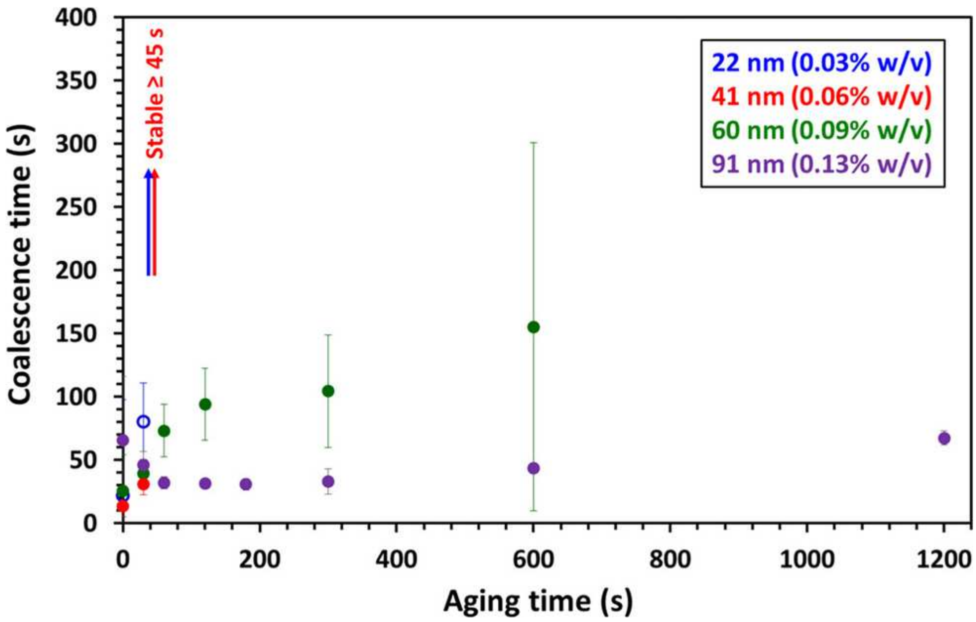

Figure 14. Coalescence time vs. ageing time plot for two *n*-dodecane droplets grown in the presence of dilute aqueous dispersions of $PGMA_{39}$–$PBzMA_x$ spheres of varying mean diameter. Open markers indicate conditions for which, in some cases, droplets were stable toward coalescence for at least 30 min. Reproduced from ref. 195 (Copyright 2017 American Chemical Society).

PICKERING NANOEMULSIONS

Nanoemulsions comprise stable oil or water droplets for which the mean droplet diameter is below 200 nm.[227-228] There are various reports of copolymer- or surfactant-stabilised nanoemulsions in the literature.[229] In contrast, there have been remarkably few examples of Pickering nanoemulsions, in which the droplets are solely stabilized by solid particles.[192-193, 230-233] No doubt one reason for the paucity of studies is the rule-of-thumb requirement that the Pickering emulsifier should be at least 5-10 times smaller than the mean droplet diameter. However, the recent development of polymerization-induced self-assembly (PISA) has enabled the highly convenient synthesis of sterically-stabilized diblock copolymer spheres of 20-25 nm diameter directly in the form of concentrated aqueous dispersions.[117, 234] In principle, such nanoparticles should constitute model Pickering emulsifiers for oil-in-water nanoemulsions.

For example, Thompson and co-workers chain-extended a water-soluble $PGMA_{48}$ precursor *via* RAFT aqueous emulsion polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) to form $PGMA_{48}$-$PTFEMA_{50}$ spheres of approximately 25 nm diameter,[192] as previously reported by Akpinar and co-workers.[234] As discussed above, the hydrophobic character of the core-forming block is of critical importance when preparing Pickering emulsions using block copolymer nanoparticles. Selecting a weakly hydrophobic block such as PHPMA usually means that the nanoparticles do not survive the high shear homogenization conditions required for droplet formation. On the other hand, nanoparticles with highly hydrophobic core-forming blocks such as PTFEMA typically remain intact and therefore can act as genuine Pickering emulsifiers. Indeed, this criterion is particularly important for the formation of Pickering nanoemulsions because even more energy-intensive conditions are required.

Initially, a Pickering macroemulsion of approximately 40 μm diameter was prepared *via* high shear homogenization of a 7.0% w/w aqueous dispersion of $PGMA_{48}$-$PTFEMA_{50}$ spheres with *n*-dodecane at 15,500 rpm. Employing a relatively high copolymer concentration during this stage was deliberate because a large excess of non-adsorbed nanoparticles was required to stabilize the nanoemulsion generated in the second stage. Such precursor emulsions were then subjected to high pressure microfluidization to generate much finer droplets (see Figure 15). The final size of the oil droplets depended on both the applied pressure and also the number of passes through the microfluidizer. At least eight passes were required to reach the minimum mean droplet diameter of 220 nm at an applied pressure of 20,000 psi.

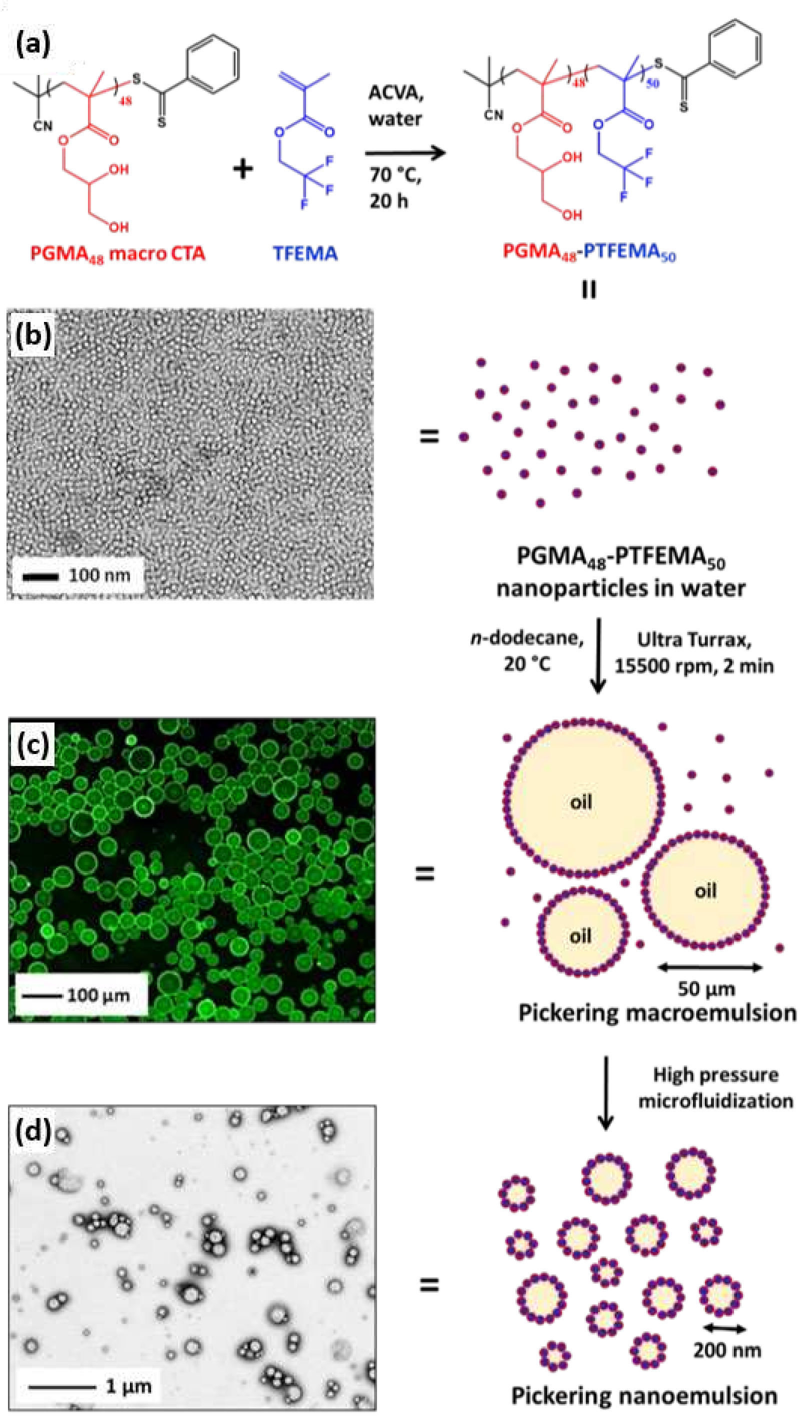

Figure 15. Schematic representation for the preparation of Pickering nanoemulsions described in this study. (a) Synthesis of $PGMA_{48}$-$PTFEMA_{50}$ nanoparticles of 25 nm diameter *via* RAFT emulsion polymerization of TFEMA using a $PGMA_{48}$ steric stabilizer; (b) TEM image of the $PGMA_{48}$-$PTFEMA_{50}$ nanoparticles; (c) fluorescence micrograph of the initial Pickering macroemulsion produced when excess nanoparticles are homogenized with *n*-dodecane for 2.0 min at 15,500 rpm. (d) This precursor macroemulsion was then further processed using a commercial LV1 microfluidizer (Microfluidics Ltd., USA) to afford a Pickering nanoemulsion (see TEM image after drying such droplets). Reproduced from ref. 192 (Copyright 2017 American Chemical Society).

Subtracting the thickness of the adsorbed monolayer of 25 nm $PGMA_{48}$-$PTFEMA_{50}$ spheres indicates a mean oil droplet diameter of less than 200 nm, which lies within the range required for a genuine nanoemulsion. Moreover, such nanoparticles enabled the formation of high internal phase nanoemulsions at oil volume fractions of up to 0.80. However, TEM analysis of dried nanoemulsion droplets prepared at 30,000 psi revealed no evidence of the original nanoparticles. At this higher applied pressure, nanoparticle dissociation occurred and the molecularly dissolved $PGMA_{48}$-$PTFEMA_{50}$ chains copolymer acted as an amphiphilic polymeric surfactant. This problem could be circumvented by incorporating EGDMA as a third block: the resulting covalently-stabilized $PGMA_{48}$-$PTFEMA_{45}$-$PEGDMA_{5}$ remained intact even at an applied pressure of 30,000 psi, thus ensuring the formation of genuine Pickering emulsions under such conditions.

In a follow-up study, Thompson et al. examined the effect of varying the oil type on the long-term stability of Pickering nanoemulsions prepared using the same $PGMA_{48}$-$PTFEMA_{50}$ nanoparticles.[193] Thus, a series of nanoemulsions prepared using four *n*-alkanes were prepared using an LV1 microfluidizer and their relative long-term stabilities were assessed using analytical centrifugation.[31] More specifically, a LUMiSizer instrument was employed to size the ageing droplets over a six-week period, see Figure 16. Significant broadening of the droplet size distribution was observed in each case, although the change in mean droplet diameter was minimal. For the more stable nanoemulsions prepared using *n*-tetradecane or *n*-dodecane, over 90% of the droplets remained below 1 μm after six weeks. Conversely, nanoemulsions prepared using *n*-octane proved to be relatively unstable, which correlates with the higher water solubility of this oil.

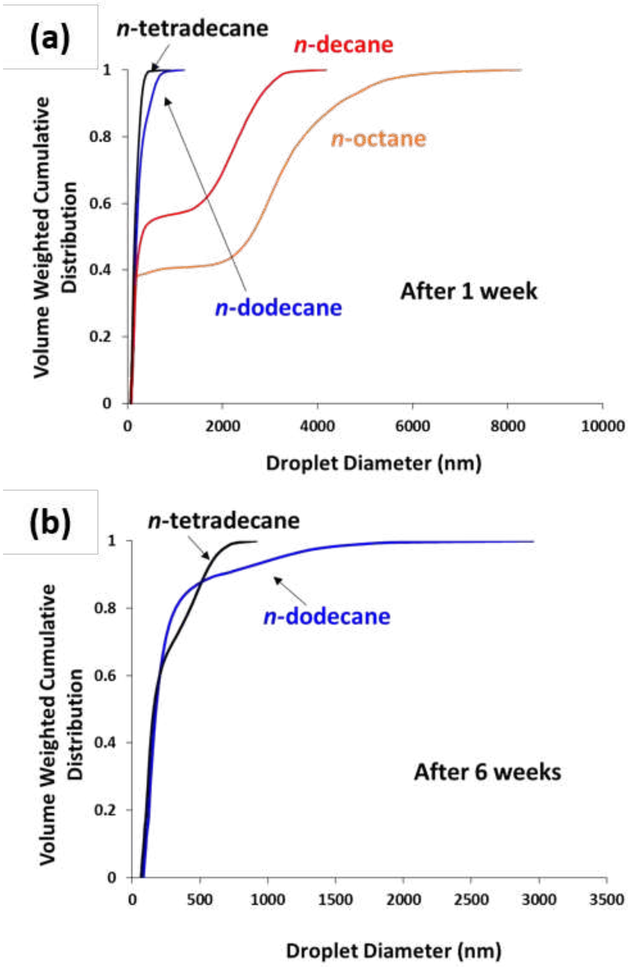

Figure 16. Volume-weighted cumulative distributions determined by analytical centrifugation (LUMiSizer instrument) for a series of four *n*-alkane-in-water Pickering nanoemulsions: (a) after ageing for one week at 20 °C and (b) after ageing for six weeks. Significant evaporation of the more volatile *n*-octane and *n*-decane oils occurred within one week so no further analysis was possible in these two cases. Reproduced from ref. 193 (Copyright 2018 American Chemical Society).

We recently explored the effect of introducing charge at the end of the steric stabilizer block on the formation and long-term stability of Pickering nanoemulsions prepared using $PGMA_{48}$-$PTFEMA_{50}$ nanoparticles.[232] RAFT-mediated PISA enables the design of block copolymer nanoparticles with minimal surface charge by simply selecting an appropriate RAFT agent when preparing the steric stabilizer precursor. Hence PGMA chains bearing either carboxylic acid, morpholine or neutral end-groups were chain-extended by RAFT aqueous emulsion polymerization of TFEMA. Thus ionization of the carboxylic acid group at neutral pH introduced terminal anionic charge, whereas protonation of the tertiary amine group at low pH conferred cationic charge. Analysis of the aqueous phase after microfluidization phase by gel permeation chromatography using a UV detector enabled convenient quantification of the nanoparticle adsorption efficiency. Up to 90% of the neutral nanoparticles were adsorbed at the surface of the oil droplets. In contrast, introducing either anionic or cationic charge at the stabilizer chain-ends significantly reduced the nanoparticle adsorption efficiency. Moreover, SAXS studies indicated that the packing efficiency of neutral nanoparticles at the oil/water interface was significantly higher than that of nanoparticles bearing charged end-groups. Analytical centrifugation was used to evaluate the long-term stability of such Pickering nanoemulsions. Pickering nanoemulsions prepared using nanoparticles bearing charged end-groups proved to be significantly less stable than those bearing neutral end-groups. Figure 17 shows droplet size distributions recorded for both freshly prepared and one-week-old Pickering nanoemulsions. If the adsorbed nanoparticles were in their neutral state, then the droplet size distribution became bimodal. On the other hand, if the same nanoparticles possessed charged end-groups then larger droplets were produced on ageing but the size distribution remained unimodal.

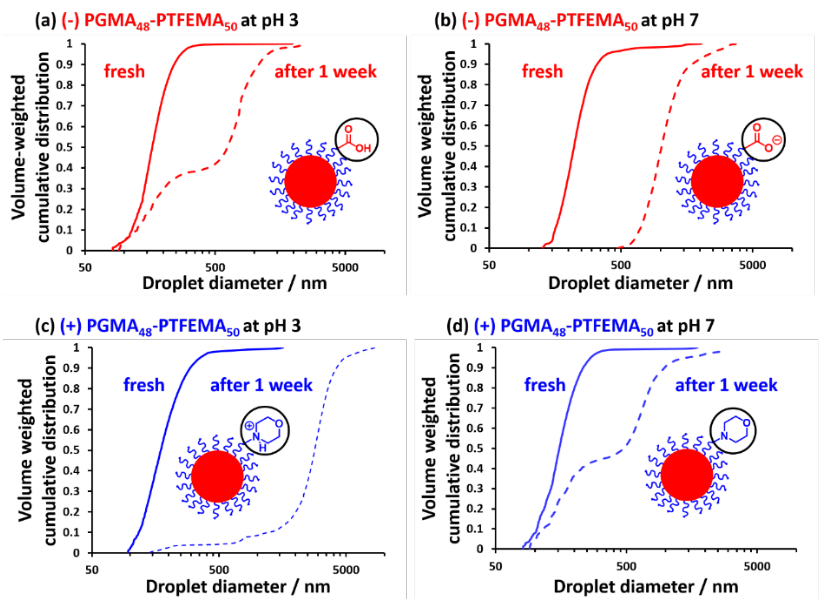

Figure 17. Volume-weighted cumulative size distributions determined by analytical centrifugation (LUMiSizer instrument) for fresh (solid line) and aged (for one week at 20 °C, dashed line) *n*-dodecane-in-water Pickering nanoemulsions prepared using 7.0% w/w $PGMA_{48}$-$PTFEMA_{50}$ nanoparticles prepared using: (a) a carboxylic acid-based RAFT agent aged at pH 3; (b) the same carboxylic acid-based RAFT agent aged at pH 7; (c) a morpholine-based RAFT agent aged at pH 3; (d) the same morpholine-based RAFT agent aged at pH 7. Microfluidizer conditions: 20,000 psi; ten passes. Reproduced from ref. 232 (Copyright 2020 American Chemical Society).

TRANSPARENT PICKERING EMULSIONS

It is well-known that emulsions usually possess high turbidity owing to strong light scattering by the droplet phase. However, according to Snell's law an emulsion should be transparent if the continuous phase and the droplet phase possess identical refractive indices.[235] For surfactant-stabilized emulsions, the emulsifier is far too small to cause any additional light scattering so examples of highly transparent conventional emulsions are not uncommon.[235-237] On the other hand, the design of transparent Pickering emulsions is much more challenging owing to additional light scattering arising from the adsorbed particles.[71, 191] In this case, the droplet phase, continuous phase and the Pickering emulsifier must possess precisely the same refractive index to eliminate light scattering and achieve high transparency. In principle, the refractive index of block copolymer nanoparticles prepared *via* PISA can be tuned by simply varying the copolymer composition. Thus, such nanoparticles are strong candidates for the design of transparent emulsions. However, the refractive index of water (1.33) lies well below that of most oils. Thus, either water-soluble or water-miscible species must be added to the aqueous phase to raise its refractive index to that of the oil phase.

In an alternative approach, Thompson and co-workers reported the preparation of an almost isorefractive *non-aqueous* Pickering emulsion using diblock copolymer worms.[71] This formulation comprised ethylene glycol-in-*n*-tetradecane emulsions stabilized by $PLMA_{16}$-$PBzMA_{37}$ worms. These two immiscible liquids were selected owing to their almost identical refractive index (~1.43). However, the core-forming PBzMA block has a relatively high refractive index of 1.57 so such emulsions are only translucent (transmittance = 70-80%, depending on the precise wavelength of visible light) owing to weak light scattering by the adsorbed worms.

Subsequently, Rymaruk et al. demonstrated that highly transparent Pickering double emulsions could be prepared by selecting a model oil, designing suitable diblock copolymer nanoparticles and employing an appropriate concentration of a water-soluble additive.[191] Semi-fluorinated PTFEMA was selected as the core-forming block owing to its relatively low refractive index of 1.42, which almost perfectly matches that of *n*-dodecane. Thus, judicious addition of either 50.5% sucrose or 67% glycerol to an aqueous dispersion of $PGMA_{56}$-$PTFEMA_{500}$ nanoparticles, followed by homogenization with *n*-dodecane, produced a highly transparent *n*-dodecane-in-water Pickering emulsion, as shown in Figure 18. Moreover, complementary water-in-*n*-dodecane Pickering emulsions of similarly high transmittance could be prepared by using hydrophobic $PLMA_{39}$-$PTFEMA_{800}$ nanoparticles prepared via PISA in *n*-dodecane. Finally, combining these hydrophilic and hydrophobic nanoparticles enabled the preparation of an o/w/o Pickering double emulsion that exhibited a mean transmittance of almost 90% across the visible spectrum. This study highlights the versatility and potential offered by PISA for the rational design of bespoke Pickering emulsifiers of tunable size and surface chemistry.

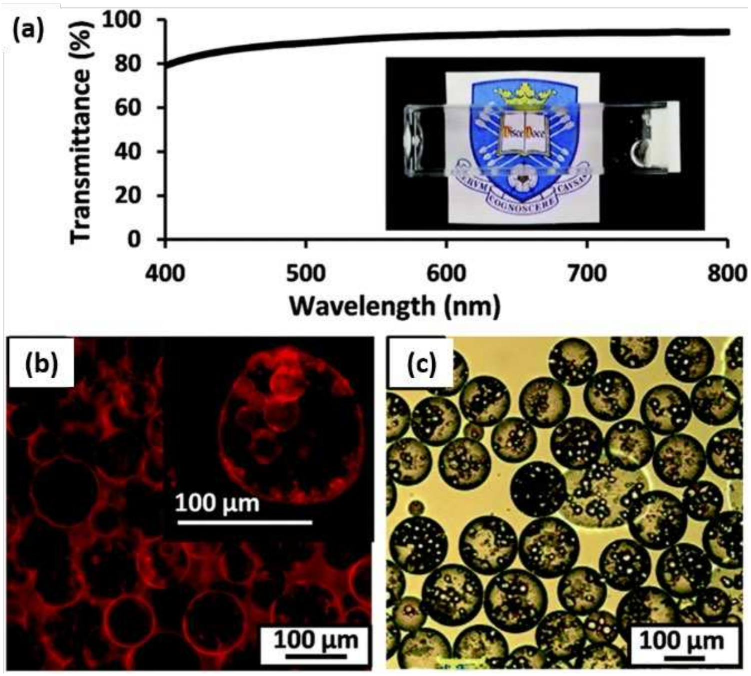

Figure 18. (a) Transmittance % vs. wavelength plot recorded for an *n*-dodecane-in-50.5% aqueous sucrose-in-*n*-dodecane Pickering double emulsion (inset: digital photograph illustrates the highly transparent nature of this refractive index-matched emulsion). (b) Fluorescence micrograph recorded for the same Pickering double emulsion prepared with Nile Red dye dissolved in the oil phase. (c) Optical micrograph obtained for the same emulsion prepared in the absence of any sucrose, i.e. with pure water, in order to provide contrast. Reproduced from ref. 191 (Copyright 2016 Royal Society of Chemistry).

CONCLUSIONS AND PROSPECT

PISA enables the facile synthesis of a wide range of block copolymer nano-objects as concentrated dispersions in either water or various oils. The particle size, copolymer morphology and surface chemistry can be predicted by selecting appropriate steric stabilizer and structure-directing blocks and targeting the desired DPs. Many of these nano-objects can be used as model polymer-based Pickering emulsifiers that can be used to examine the effect of varying the particle size, morphology, surface roughness and surface charge. In principle, this enables the effect of varying such parameters on the interfacial surface tension, adsorption dynamics, interparticle forces and interfacial mechanics to be examined, although such model experimental studies are yet to be performed. In some cases, such Pickering emulsifiers may be prone to dissociate into individual amphiphilic copolymer chains during high shear homogenization. However, this technical problem can be addressed by either covalent stabilization or addition of a more solvophobic block such as PBzMA.[72, 187-188, 194 117] Recently, we have reported protocols for preparing sphere, worms and vesicles via RAFT aqueous emulsion polymerization of vinyl monomers that exhibit moderate aqueous solubility (15-20 g dm^{-3}).[238-240] Such nano-objects are expected to act as new Pickering emulsifiers that are stable towards high shear emulsification without recourse to covalent stabilization. RAFT aqueous emulsion polymerization has also enabled the synthesis of relatively small block copolymer nanoparticles possessing highly hydrophobic cores. Such nanoparticles can be used to prepare model *n*-alkane-in-water Pickering nanoemulsions.[192] This has enabled systematic studies of the effect of varying (i) the *n*-alkane type[193] and (ii) the introduction of terminal ionic charge[232] on the rate of demulsification via Ostwald ripening. For example, using a suitably hydrophobic stabilizer block such as poly(lauryl methacrylate) or poly(stearyl methacrylate) should enable the formation of the analogous *water-in-oil* Pickering nanoemulsions if an *n*-alkane-insoluble core-forming block such as

PBzMA[158] or PTFEMA[241] confers sufficient stability to prevent *in situ* degradation during microfluidization. Indeed, we have just exemplified this concept.[242] Remarkably, PISA has also enabled the preparation of transparent Pickering double emulsions.[191] More specifically, the refractive index of the nanoparticle emulsifier can be tuned by selecting an appropriate core-forming block to match that of the chosen oil, with the refractive index of the aqueous phase being subsequently tuned by addition of a suitable water-soluble additive (e.g. sucrose or glycerol). Such studies highlight the rational design capability afforded by PISA for the preparation of a wide range of block copolymer nanoparticles to act as bespoke Pickering emulsifiers. This versatility augurs well for potential commercial applications of this technology.

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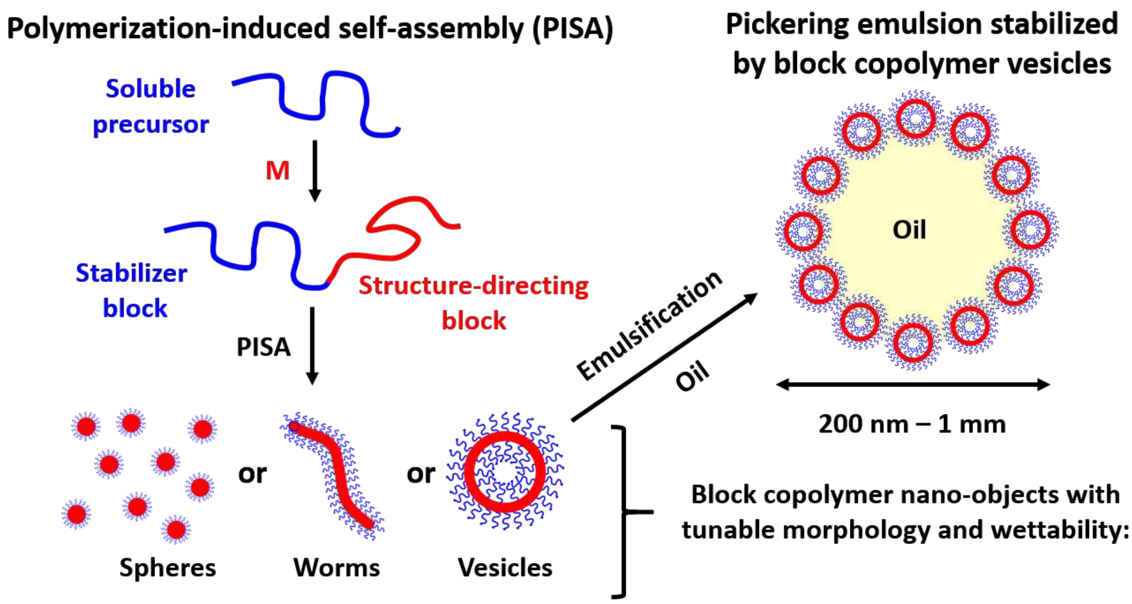
TOC graphic


Polymerization-induced self-assembly (PISA)
Soluble precursor
M
Stabilizer block
Structure-directing block
PISA
or
or
Spheres
Worms
Vesicles
Emulsification
Oil
Pickering emulsion stabilized by block copolymer vesicles
Oil
200 nm – 1 mm
Block copolymer nano-objects with tunable morphology and wettability:

Author Biographies

Prof. Steven P. Armes received his BSc (1983) and PhD (1987) Chemistry degrees from the University of Bristol and worked as a post-doctoral fellow at Los Alamos National Laboratory in New Mexico (1987-89). He accepted a lectureship at Sussex University in 1989 and was promoted to full Professor in 2000. He moved to the University of Sheffield in 2004. He works at the interface of synthetic polymer chemistry and colloid science and has published more than 650 papers to date (H-index 113) His research interests include block copolymer self-assembly, polymerization-induced self-assembly, Pickering emulsions, colloidal nanocomposite particles, microgels, gels, foams, and conducting polymer particles for space science applications.

Saul J. Hunter is a current PhD student working in the Armes group at the University of Sheffield. He was awarded the Haworth prize and medal when graduating top of his class with an MChem degree in Chemistry from the same institution in 2017. His EPSRC-sponsored research project is focused on Pickering (nano)emulsions and is partially supported by DSM (The Netherlands). He has co-authored four publications to date, including two papers in *Langmuir*, and he expects to receive his PhD degree by the end of 2021.