Polymers with advanced architectures as emulsifiers for multi-functional emulsions

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REVIEW

Polymers with advanced architectures as emulsifiers for multi-functional emulsions

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Emulsions have wide applications in the food, cosmetics, and pharmaceutical industries. Emulsions stabilized with polymers having different architectures, such as linear diblock and triblock copolymers, branched polymers, star polymers, graft polymers, and densely grafted bottlebrush polymers, have been used for encapsulation, delivery, and as templates for polymerization reactions. Stimuli-responsive polymers have been used for on-demand demulsification and emulsion engineering. In this review, we highlight the developments in the past decade that used polymers with advanced architectures as multi-functional emulsifiers.

1. Introduction

Emulsions, where one or more liquid phases are dispersed in another continuous liquid phase, have wide applications in the food, cosmetics, and pharmaceutical industries.[1-16] Emulsions responsive to external stimuli, such as light,[17] temperature,[18-21] pH,[22-32] CO_2,[33-37] redox reactions,[38-40] magnetic field,[41,42] ions,[43] or a combination of these stimulus,[44-48] have been designed for different applications, including the processing of crude oil, and the recycling and reusing of encapsulated catalysts.[14,49-51] Emulsions are also widely used as templates for polymerization[52-54] where either the dispersed phase or the continuous phase can be polymerized to give spherical latexes[55-57] or porous materials.[58,59]

Unlike solutions that are homogeneous and stable, emulsions are usually thermodynamically unstable. Coalescence, which refers to the merging of different droplets driven by the minimization of the interfacial area, is a primary route for emulsions to degrade. Ostwald ripening also contributes to the destabilization of emulsions.[60-63] Amphiphilic small molecules and linear diblock copolymers have been used as conventional emulsifiers to lower the interfacial energy and prevent coalescence so that the emulsions can be kinetically stabilized for sufficient time. Pickering emulsifiers, particles with intermediate hydrophobicity that can absorb at the interface to screen the interfacial area and protect the emulsions against coalescence, are also widely studied.[14,51,64-68] Compared with small molecule emulsifiers, Pickering emulsifiers give better biocompatibility and recyclability. Janus Pickering emulsifiers, where two sides of the particles have opposite wettability, provide even higher emulsification efficiency due to the amphiphilicity and high binding energy of the particles to the interface.[69]

There are many factors to consider when designing an emulsifier for specific applications, such as droplet size, type of emulsion, the volume ratio between two phases, emulsion stability, and the ability for on-demand demulsification, recyclability, and reusability of both the emulsifiers and the species encapsulated in the emulsions. Polymers are prime candidates as emulsifiers due to their structural versatility. Droplet size can be controlled by emulsifier concentration since more emulsifiers can cover a larger interfacial area and give smaller droplets.[70] Polymer chains with lower compactness and higher conformational flexibility will also cover a larger interfacial area for the same concentration of emulsifiers to give smaller droplets.[71] There are several types of emulsions, such as simple emulsions like oil-in-water emulsions (o/w) and water-in-oil emulsions (w/o), multiple emulsions like oil-in-water-in-oil emulsions (o/w/o) and water-in-oil-in-water emulsions (w/o/w),[72] bicontinuous emulsions,[73,74] etc. It has been found that hydrophilic emulsifiers favor the formation of o/w emulsions and vice versa.[65] The degree of hydrophilicity or hydrophobicity of emulsifiers can be quantitatively described by the “hydrophilic-lipophilic balance”, usually ranging from 0 to 20 and increasing with the hydrophilicity of emulsifiers.[75] In some cases, phase inversion can simply be achieved by changing the volume ratio between the two phases.[72] Creaming and sedimentation,[76,77] the migration of the droplets to the top or bottom of the emulsion due to density differences, can increase the local volume fraction of the dispersed phase. High internal phase emulsions (HIPEs), emulsions having a dispersed phase volume fraction higher than spatial occupancy of densely packed uniform spheres (74%), can be achieved with emulsifiers that are completely insoluble in the dispersed phase,[78] or emulsifiers that possess significantly different compactness between the hydrophilic and hydrophobic blocks, for example, poly(poly(ethylene glycol) methyl ether acrylate)-*block*-polystyrene.[79]

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Polymers can either be used as conventional emulsifiers with great conformational flexibility or Pickering emulsifiers with particulate self-assemblies. Compared with amphiphilic diblock copolymers, where the repeating units are connected linearly without any branches, polymers with advanced architectures have been achieved with the development of synthetic methodologies. They have opened possibilities to fine-tune properties of emulsions to meet the needs of various applications. Branched polymers, which have several branching units introduced to the linear polymer chains, showed higher emulsion stability than their linear analogs due to the steric hindrance and multipoint irreversible anchoring at the oil-water interface.[80] Star polymers have linear polymer chains connected to a central core.[81-87] Depending on the number of arms, star polymers can either behave like linear A-B-A type Gemini emulsifiers or particle-like Pickering emulsifiers.[88] Wettability towards the oil and aqueous phase can be tuned by the composition of miktoarm star polymers with mixed hydrophilic and hydrophobic arms.[70] Graft copolymers with a flexible backbone and amphiphilic side chains can be used as conventional emulsifiers due to the opposite wettability of different side chains.[89] Graft copolymers with a rigid backbone, like cellulose nanocrystals (CNCs), or with self-assembled core-shell micelles, can be used as Pickering emulsifiers.[90] When the grafting density is high, the steric hindrance of side chains forces the polymer backbone to extend and give a bottlebrush conformation.[91-96] Bottlebrush copolymers have high emulsification efficiency and can even significantly enhance the interfacial dilatational modulus of the emulsion droplets.[97] In this review, we summarized the developments in the past decade using polymers with different architectures as emulsifiers at the oil-water interface.

2. Polymers with different architectures as emulsifiers

2.1 Polymersomes assembled with block copolymers

Polymersomes, also known as block copolymer vesicles, refer to hollow vesicular structures formed from bilayer membranes of amphiphilic block copolymers.[98] The structural integrity of polymersomes with low permeability makes them good candidates to stabilize water-in-water and oil-in-oil emulsions. With the well-known biphasic systems of the aqueous solutions of polyethylene glycol (PEG) and dextran, Fletcher *et al*. stabilized water-in-water emulsions using a poly[poly(ethylene glycol) methyl ether methacrylate]-*block*-poly (n-butyl methacrylate)-*block*-poly[2-(dimethylamino) ethyl methacrylate] triblock copolymer, where the hydrophobic middle block facilitated the formation of polymersomes and prevented coalescence of the aqueous dropltes.[99] Lecommandoux *et al*. successfully loaded different liposomes into the lumen of the same polymersome formed with poly(butadiene)-*block*-poly(ethylene oxide) (PB-*b*-PEO), mimicking the multicompartmentalization in a biological cell.[100] Lodge *et al*. developed oil-in-oil emulsions with $CHCl_3$ solutions of polystyrene (PS) and PB homopolymers. The oil-in-oil emulsions were stabilized with polymersomes co-assembled with PS-*b*-PEO and PB-*b*-PEO, where the $CHCl_3$-insoluble PEO blocks formed a membrane at the interface and the PS and PB blocks faced the PS-rich and PB-rich oil phases accordingly.[101]
Compared with the above examples where the dispersed phase of the emulsion was encapsulated in the interior (lumen) of each polymersome, using polymersomes as Pickering emulsifiers to stabilize o/w and w/o emulsions post a greater challenge to the structural integrity of polymersomes **(Fig. 1a)**.[102] The homogenization process used to produce emulsions is usually challenging for non-crosslinked polymersomes to survive, so the resultant emulsion is stabilized by individual amphiphilic block copolymers, instead of polymersomes. However, cross-linked polymersomes can preserve their structural integrity during homogenization and act as Pickering emulsifiers.[102] Pickering emulsions stabilized by polymersomes have tremendous versatility for encapsulation and biphasic catalysis, compared with emulsions formed from linear diblock copolymers since the low permeability of the bilayer membrane

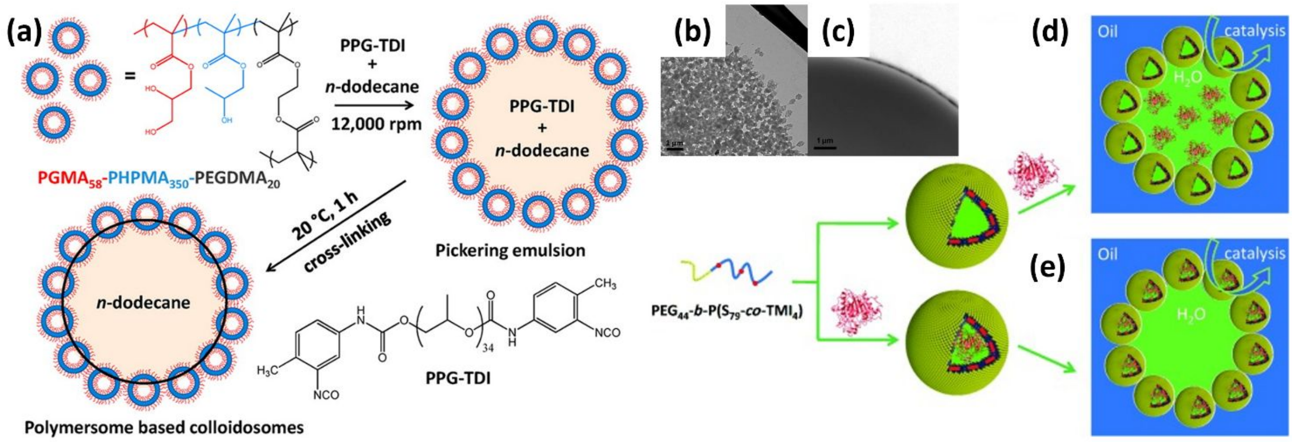
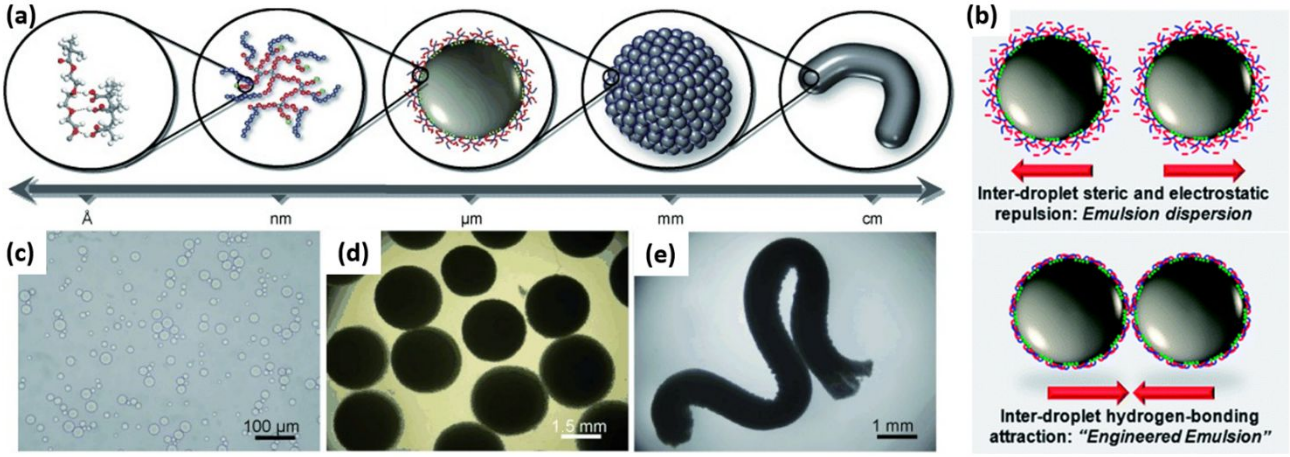


Figure 1. (a) Schematic representation of the preparation of cross-linked polymersomes and colloidosomes. (b) and (c) TEM images of cross-linked colloidosome surfaces prepared with (b) cross-linked polymersomes and (c) linear polymersomes. Adapted with permission from American Chemical Society (ref. 102), Copyright (2012). (d) and (e) Schematic representation of a Pickering emulsion with the enzyme encapsulated in the dispersed aqueous phase (d), or inside the polymersome lumen (e). Adapted with permission from John Wiley and Sons (ref. 103), Copyright (2012).

towards macromolecules enable encapsulation of different species in the dispersed phase and the interior (lumen) of each polymersome at the same time.[103]

Armes *et al*. first showed that polymersomes could stabilize *n*-dodecane-in-water Pickering emulsions **(Fig. 1a)**.[102] The polymersomes were prepared by the *in situ* self-assembly of poly(glycerol monomethacrylate)-*block*-poly(2-hydroxypropyl methacrylate) (PGMA-*b*-PHPMA) during aqueous dispersion polymerization, followed by the addition of ethylene glycol dimethacrylate (EGDMA) as a crosslinker to preserve the structural integrity of polymersomes. Transmission electron microscopy (TEM) images of the colloidosomes formed with the addition of an oil-soluble diisocyanate showed that the cross-linked polymersomes survived homogenization and gave stable o/w Pickering emulsions **(Fig. 1b)**. In comparison, the un-crosslinked polymersomes failed **(Fig. 1c)**. van Hest *et al*. developed water-in-toluene Pickering emulsions stabilized by crosslinked poly(ethylene glycol)-*block*-poly(styrene-*co*-3-isopropenyl-α,α-dimethyl-benzyl isocyanate) (PEG-*b*-P(S-*co*-TMI)) polymersomes. The Pickering emulsion was used for enzyme-catalyzed esterification. The enzyme was either encapsulated in the dispersed aqueous phase when it was added to the aqueous solution prior to emulsification **(Fig. 1d)**, or the interior (lumen) of each polymersome when it was added to the THF solution of block copolymers prior to formation of the polymersomes **(Fig. 1e)**.[103] With substrates in the oil phase, enzymes encapsulated in the lumens had higher specific activity due to the concentrated distribution at the oil-water interface. The same group also developed pH-responsive water-in-ethyl acetate Pickering emulsions stabilized with cross-linked polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) polymersomes.[104] The hydrophilicity of PAA blocks significantly increased upon increasing pH, enabling base-triggered demulsification when the polymersomes detached from the oil-water interface. With the strong affinity between PAA and nanoparticles, one side of the polymersomes exposing to the aqueous phase could be selectively modified with Au or Pt nanoparticles followed by demulsification to produce Janus polymersomes.



2.2 Branched copolymers

Compared with linear polymers, branched copolymers have repeating units covalently connected to another polymer chain. Weaver *et al*. developed a variety of branched copolymer surfactants (BCSs) that gave much higher emulsion stability in comparison to their linear analogs, due to their wider globular morphologies and multi-site anchoring at the oil-water interface, as shown in **Fig. 2a**.[80,105,106] The BCSs not only stabilized dodecane-in-water emulsions but also opened the possibility for emulsion engineering, where the inter-droplet interactions significantly enhanced the mechanical strength and trapped the emulsions in self-supporting geometries, such as molded shapes, spheroidal and fibrillar assemblies. Furthermore, pH-responsive inter-droplet interactions enabled a rapid switching between an engineered emulsion and a free-flow emulsion without significant coalescence, due to the high stability of the BCSs emulsions.

Two different approaches towards pH-responsive inter-droplet interactions, hydrogen-bonding **(Fig. 2b)** and electrostatic forces, have been exploited for emulsion engineering.[80,107] The BCSs with inter-droplet hydrogen-bonding consisted of hydrophobic dodecane chain ends and two hydrophilic repeating units, methacrylic acid (MAA) and poly(ethylene glycol) methacrylate (PEGMA). PEGMA always acted as a hydrogen bond acceptor, while MAA acted as a hydrogen bond donor only in acidic environment.[106,107] As a result, the emulsion droplets were dispersed at high pH **(Fig. 2c)** and assembled in an acidic environment. Spheroidal assemblies could be achieved by dripping the emulsion into acidic water **(Fig. 2d),** and fibrillar assemblies could be achieved by extruding the emulsion below the surface of acidic water **(Fig. 2e)**. Instead of HCl, which has limited diffusivity when added to the emulsions, the slow hydrolysis of glucono-δ-lactone in aqueous solution could homogeneously reduce the pH, thus enabling the molding of much larger structures.[108] Furthermore, Fe_3O_4 nanoparticles could be encapsulated in the oil phase to give magnetic molded shapes.[109] The BCSs with inter-droplet electrostatic forces also consisted of dodecane chain ends. Two different BCSs containing 2-(sulfobenzoic acid) ethyl methacrylate (SHEMA) or 2-(dimethylamino) ethyl methacrylate (DMA) as repeating units were separately prepared then mixed. SHEMA was always negatively charged, while DMA was positively charged only in an acidic environment.[107]

In addition to emulsion engineering, the BCSs were also used for emulsion-based encapsulation. For example, encapsulation could be achieved by mineralization of calcium phosphate at the surface of the emulsion droplets, where the carboxylic groups of MAA were used as nucleating sites, due to their ability to chelate Ca^{2+}.[110] The encapsulation could also be achieved by cross-linking at the surface of the droplets by the self-condensation of silanol groups incorporated in the BCSs.[111] Besides emulsion-based encapsulation, Rannard *et al*. recently proved the BCSs with similar chemical structures as a new candidate for drug delivery. Protease inhibitor lopinavir had a high permeability when applied to an epithelium monolayer in nanoemulsions stabilized with the BCSs.[112] Thiol-functional emulsions stabilized with the BCSs were mucoadhesive and showed mucus triggered release, opening possibilities for drug delivery.[113]

Besides synthetic BCSs, a lot of natural BCSs are used in the food industry as sustainable emulsifiers with bioactivity, biocompatibility, and biodegradability, for example, gum Arabic which is based on highly branched polysaccharide.[114] Corn fiber gum, majority of which is also highly branched polysaccharide, is believed to be a promising substitution for gum Arabic.[115,116] The branch architecture afforded these natural macromolecules with small radius of hydration thus low viscosity of their solutions.[114] Waxy rice starch, which mostly contains highly branched amylopectin, can also be used as emulsifiers after gelatinization.[117,118]

2.3 Star polymers

Star polymers refer to the structures where multiple polymer chains are connected to one core. The core can be either a cross-linked hardcore like polydivinylbenzene (PDVB) or a well-defined multi-functional small molecule. The arms could be either uniform or a mixture of different polymers, known as miktoarm star copolymers. Multiple approaches have been used to tune the amphiphilicity of star copolymers, including the variation of the ratio between different arms[70] or the pH, thus the degree of protonation of the polyelectrolyte arms.[119]

By tuning the amphiphilicity, different types of emulsions have been achieved, such as simple emulsions like o/w or w/o, or multiple emulsions like o/w/o or w/o/w.

By comparing the o/w emulsions with xylene or cyclohexane as the oil phase of poly(ethylene oxide) (PEO) linear and star polymers with crosslinked PDVB core, Tilton *et al*. showed that star polymers had a higher degree of absorption, yielded a lower interfacial tension and a higher dilatational elasticity due to their structural compactness.[120] Furthermore, star polymers could also induce spontaneous emulsification to give water-in-xylene emulsions if the PEO star polymers were first dispersed in the xylene phase, due to the Marangoni flow created by nonuniformities in the local interfacial tension. An *et al*. synthesized core-crosslinked star polymers with three different hydrophilic arms, poly(N,N'-dimethyl acrylamide) (PDMA), poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA), and poly(2-methoxyethyl acrylate-*co*-poly(ethylene glycol) methyl ether acrylate) (P(MEA-*co*-PEGA)), that could stabilize toluene-in-water or benzene-in-water emulsions.[121] Jin *et al*. synthesized 4-arm star polymers with a porphyrin core and hydrophilic arms.[122] The arms were composed of poly(methyloxazoline)-*block*-poly(ethyl oxazoline) (PMOX-*b*-PEOX) diblock copolymers with a strongly hydrophilic PMOX block and a weakly hydrophilic PEOX block. The color of the porphyrin enabled visualizing the assembly of the star copolymers at the chloroform-water interface. The emulsion was used as a template for sol-gel reactions of tetraethyl orthosilicate (TEOS) to prepare hollowed spheres.

The effect of arm length and arm numbers on the properties of emulsions, such as droplet size, interfacial tension, and internal phase fraction, have been systematically investigated. Matyjaszewski *et al*. developed core-crosslinked star polymers with uniform arms of PEO or mixed arms of PEO and poly(butyl acrylate) (PBA).[70] Hydrophilic PEO arms gave o/w emulsions with xylene as the oil phase while with PBA introducing hydrophobicity to the miktoarm copolymers, w/o emulsions were obtained, as shown in **Fig. 3**. Star polymers with uniform, loosely packed arms resulted in lower interfacial energy than densely packed arms, due to better exposure of the hydrophobic core to the oil phase. Li and Wang *et al*. synthesized star polymers with hexa(eugenol) cyclotriphosphazene (HECTP) core and precisely controlled the number of PEG arms.[88] In comparison to stars with two arms, which are more like Gemini surfactants, stars with 4 or 6 arms are more like Pickering surfactants and could stabilize xylene-in-water HIPEs. It turned out the star polymers with less and shorter arms gave a lower surface tension and higher emulsification efficiency due to the lower compactness of the polymers and higher flexibility to reconfigure to expose the hydrophobic core to the oil phase. The impact of arm length and number on the emulsion type (simple emulsion or multiple emulsion) was investigated by Ma *et al*., where star polymers with the number of poly(lactic acid) (PLA) arms ranging from 2 to 64 were synthesized.[123] The arms were soluble in THF. The hydroxyl groups at the end of each arm and the unreacted sites of the initiator core have high affinity with the glycerol phase, imparting the star polymers with interfacial activity. The star polymers with higher hydroxy densities favored complicated double or multiple emulsions with larger interfacial areas in comparison to simple THF-in-glycerol emulsions.

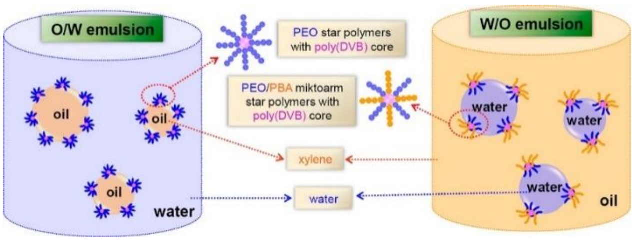


Figure 3. Schematic representation of star polymers with uniform PEO arms or mixed PEO/PBA arms as stabilizers for o/w or w/o emulsions. Reproduced with permission from American Chemical Society (ref. 70), Copyright (2012).

Functional arms were widely used to impart stimuli-responsiveness to star polymers. An *et al*. synthesized pH-responsive core-crosslinked star polymers containing poly(N,N-dimethyl aminoethyl methacrylate) (PDMAEMA) as the arms.[119]

At high pH, the arms were deprotonated and gave w/o emulsions due to the better solubility of the arms in the toluene phase. At lower pH, the arms were protonated, and the hydrophilicity increased, which gave intermediate o/w/o and w/o/w multiple emulsions and finally o/w HIPEs. P(MEA-*co*-PEGA), which is responsive to salt and temperature, was used as the arms for dual responsive star polymers.[124] Demulsification of the dodecane-in-water HIPEs could be achieved upon heating above the lower critical solution temperature (LCST) of the arms. The stability of the emulsion and demulsification efficiency could be tuned by the addition of kosmotropes and chaotropes. The kosmotropes reduced the cloud point and enhanced the demulsification efficiency while the chaotropes raised the cloud point and enhanced the thermal stability of the emulsions. Gao *et al*. synthesized dual responsive Y-shaped AB_2 miktoarm star copolymers with two hydrophilic PDMAEMA arms and one hydrophobic PS arm.[72] The star copolymers could stabilize both o/w and w/o emulsions with toluene as the oil phase depending on the volume ratio. Demulsification could be triggered with increasing pH, and phase inversion from o/w to o/w/o emulsion could be achieved upon heating under moderate stirring.

Supramolecular chemistries offered another approach to core-crosslinked structures. Gao *et al*. synthesized β-cyclodextrin-terminated poly(N-isopropyl acrylamide) (PNIPAM-β-CD) and azobenzene-capped poly(4-vinyl pyridine) (P4VP-azo) that formed supramolecular diblock copolymers through the inclusion interaction between the β-CD host and the azobenzene guest then self-assembled into core-shell polymer particles in the aqueous phase followed by cross-linking of the P4VP core.[125] The core cross-linked supramolecular polymer particles could stabilize o/w emulsion with styrene, benzene, or chloroform as the oil phase. The PNIPAM shells would collapse upon heating, thus triggering demulsification, imparting thermal responsiveness to the emulsions. The emulsions also had light- and competitive guest-responsiveness. The supramolecular linkages between the core and the shell could be cleaved by the UV-induced transition from *trans*-azobenzene to *cis*-azobenzene, the latter of which does not bind with β-CD. The linkages could also be cleaved with the addition of a guest with a higher binding affinity with β-CD so that the azo groups were expelled.

Compared with previously summarized research that used individual star polymers as emulsifiers, Yuan and Wang *et al*. used two different 8-arm PEG star polymers end-functionalized with CD or ferrocene (Fc) groups to form microgels via host-guest interactions, as shown in **Fig. 4**.[39] The microgels could stabilize o/w Pickering emulsions with hexane as the oil phase. The host-guest interaction could be cleaved with oxidation potential stimulus and reformed with a reduction potential stimulus. The Pickering emulsion was used for enzyme-catalyzed reactions, where the stimulated demulsification enabled convenient product separation and enzyme recycling.

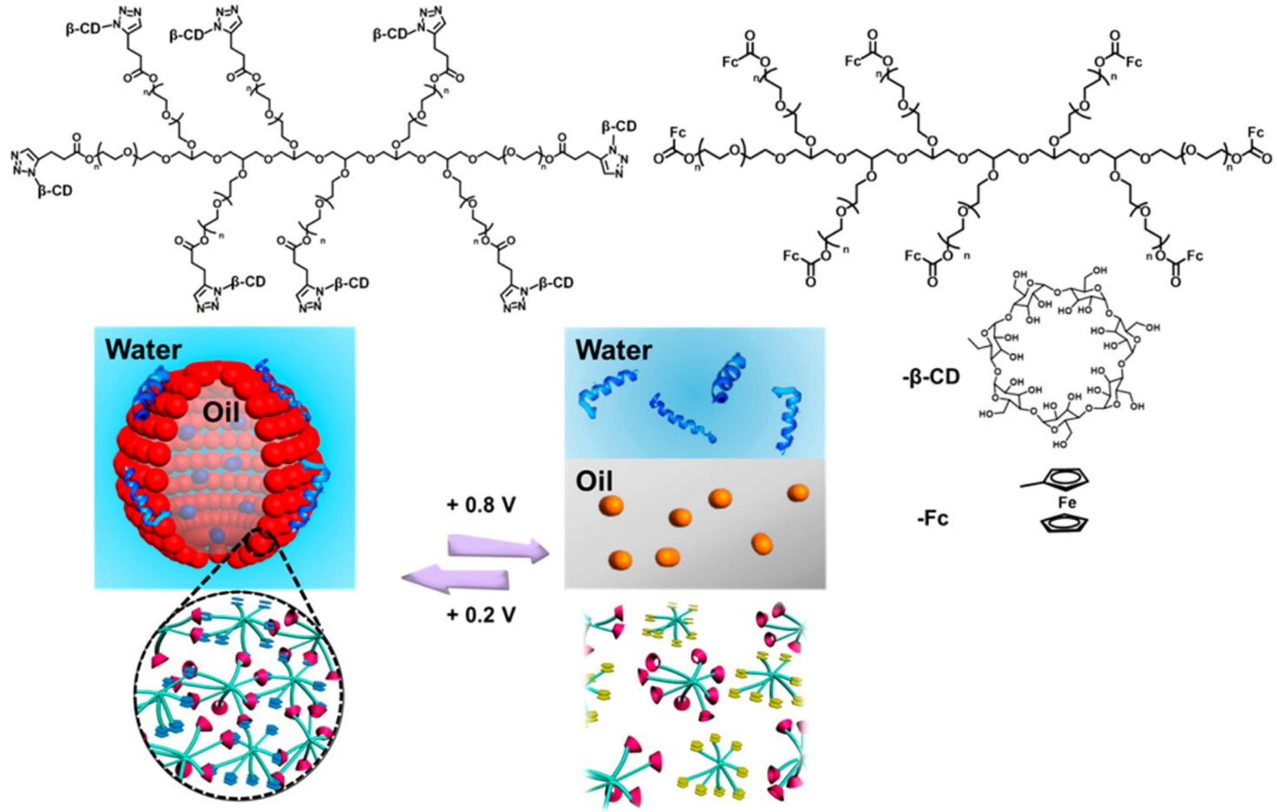
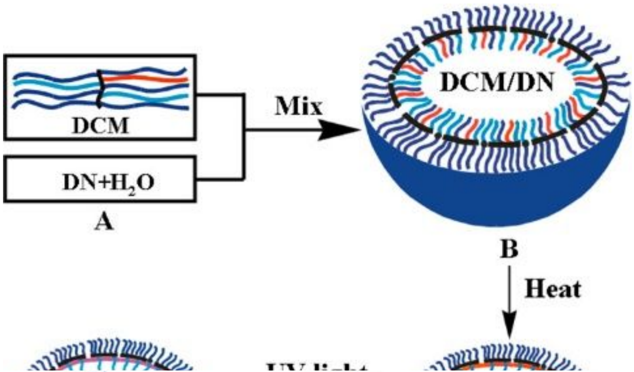


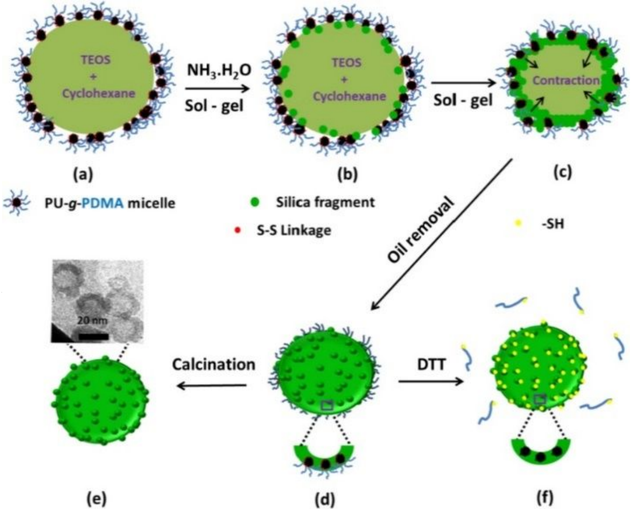
Figure 4. Molecular structures of 8-arm PEG-CD and 8-arm PEG-Fc, and schematic representation of the potential-responsive assembly and disassembly of the microgels. Adapted with permission from American Chemical Society (ref. 39), Copyright (2016).

In addition to acting as emulsifiers at the oil-water interface, star polymers could also serve as interfacial connectors for gels, for example, core-crosslinked miktoarm star copolymers containing PBA and poly ((oligo (ethylene glycol) methacrylate) (POEGMA) as the arms developed by Matyjaszewski *et al*.[126] Two layers of consecutively synthesized gels could be mechanically connected with the star polymers acting as an interfacial compatibilizer and sufficient diffusivity of the monomer of the secondly synthesized layer.

2.4 Graft polymers

Amphiphilic graft copolymers with flexible backbones could be used as conventional emulsifiers. For example, ternary graft copolymers have three different polymer chains grafted onto a polymer backbone. One of the grafts is hydrophilic, and another one is hydrophobic to ensure strong absorption at the oil-water interface. Crosslinking of the third graft could enhance the structural integrity for the encapsulation of nanoparticles and drugs. Hu *et al.* synthesized a series of ternary graft copolymers by click chemistries, which stabilized decahydronaphthalene-in-water (DN-in-water) emulsions. The ternary graft copolymers could be divided into two categories according to the solubility of the third graft. A third graft soluble in neither oil nor water could form a thin membrane and separate the two phases, which, after cross-linking, could further stabilize the emulsion, as shown in **Fig. 5**.[89,127] A third graft soluble in the aqueous phase could give partially cross-linked coronas.[128,129]





In the first category, water-soluble poly(ethylene glycol) methyl ether (MPEG), oil-soluble PS, and a third poly(2-cinnamoyloxyethyl methacrylate) (PCEMA) polymer chain, which is soluble in neither oil nor water, were grafted onto the polymer backbone. The MPEG and PS chains extended into aqueous and oil phase accordingly, and PCEMA chains formed a thin membrane at the oil-water interface followed by photo-crosslinking.[89] Fe_3O_4 nanoparticles could be encapsulated in the oil phase so that the capsules could be captured by external magnetic field then redispersed by shaking without significant deterioration.[127]

In the second category, water-soluble PAA was used instead of PCEMA and cross-linked with diamine.[128] Since both PAA and MPEG are water-soluble, nanocapsules with partially cross-linked coronas were obtained. The permeability of the nanocapsules could be tuned by changing the ratio between PAA and MPEG. Furthermore, PAA imparted the emulsion with pH responsiveness, where demulsification could be triggered by decreasing pH. The emulsion was used for in-cell releasing of doxorubicin, due to the comparatively low pH of cytosols.[129]

In addition to conventional emulsifiers, graft copolymers can also self-assemble into micelles and act as Pickering emulsifiers. Gao *et al.* synthesized polyurethane-*graft*-poly(N,N-dimethyl acrylamide) (PU-*g*-PDMA) with hydrophobic PU backbone and hydrophilic PDMA side chains.[90] The graft copolymers could self-assemble in the aqueous phase to form core-shell micelles that could later stabilize toluene-in-water Pickering emulsions when the aqueous dispersion of the micelles was homogenized with toluene. The micelles were supposed to hold their structural integrity and act as Pickering emulsifiers since the cores of the micelles were insoluble in water and oil. The same group also connected the PMDA side chains to the PU backbone by cleavable S-S linkages, which imparted redox-responsiveness.[130] The cyclohexane-in-water Pickering emulsion stabilized by the micelles could be demulsified by reducing agents, for example, dithiothreitol. The Pickering emulsion stabilized with redox-responsive PU-*g*-PDMA was then used as a template for interfacial sol-gel reactions to prepare hollowed SiO_2 microspheres, as shown in **Fig. 6**.[131] Mixtures of TEOS and cyclohexane were used as the oil phase, and the sol-gel reaction was triggered by pH adjustment. Since the hydrophobic PU cores preferentially segregated to the oil-water interface, they were entrapped in the formed SiO_2 layers. Cleavage of the S-S bonds left many thiol groups at the surface of the hollowed sphere, which could later be used for adsorbing toxic metal ions, for example, Pb^{2+}.

Compared to synthetic graft copolymers, CNCs are rigid prolate spheroidal crystals and always behave as Pickering emulsifiers. CNSs also have several advantages, such as availability from natural sources, biodegradability, and environmental compatibility. CNCs prepared with sulfuric acid hydrolysis of cellulose are hydrophilic and are easily dispersible in the aqueous phase. The surfaces of CNCs are negatively charged due to the anionic sulfate half-ester groups.[132] The inherent negative charge precludes the adsorption of the CNCs to the oil/water interface.[133] The electrostatic interaction between surface charges could be screened by salt or reduced by functionalization.

There are generally two methods to modify CNCs with polymers, where the polymer chains are chemically connected or physically absorbed on the surface of CNCs. With the hydroxy groups on the surface, end-functionalized polymer chains could be grafted onto the CNCs, and polymer chains could be grafted from the CNCs by polymerization reactions, such as nitroxide-mediated radical polymerization (NMP), reversible addition–fragmentation chain-transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP).[134] Physical absorption of polymers, for example, hydroxyethyl- or methyl-cellulose, could also be used to enhance emulsification efficiency.[135,136] CNCs modified with responsive polymers gave emulsions where on-demand demulsification could be achieved with temperature, pH, and CO_2.[137-139] The emulsions stabilized by polymer-modified CNCs have broad applications, including emulsion polymerization[140] and the production of HIPEs gels.[141] We summarize the recently published works about polymer-grafted CNCs as emulsifiers at the oil-water interface.

Emulsions stabilized with polymer-grafted CNCs were widely used for polymerization reactions, which could be performed in either the dispersed phase of the emulsion to give polymer latexes or the continuous phase to provide microporous hydrogels. In the former case, Wang and Chen *et al*. synthesized poly(vinyl tetrazole-*random*-butyl acrylate) grafted CNCs (P(VT-*r*-BA)-*g*-CNC, where random copolymers have higher functional group densities in comparison to end-functionalized polymer chains.[140] The hydrophobicity of BA groups of the grafted side chains were essential to stabilize the Pickering emulsions. Methyl methacrylate-in-water (MMA-in-water) Pickering emulsions could be stabilized, followed by polymerization to give spherical PMMA particles. Styrene-in-water Pickering emulsions stabilized by polymer-grafted CNCs were reported by Ni *et al*.[142] and Cunningham *et al*.[143] for emulsion polymerization to prepare PS particles. In the latter case, Wang *et al*. synthesized poly(2-(3-(6-Methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl methacrylate) methacrylate) grafted CNCs (CNC-*g*-PUPyMA), which were used to stable dodecane-in-water HIPEs.[141] HIPEs-templated microporous hydrogels were prepared through polymerization in the continuous aqueous phase. The PUPyMA not only introduced hydrophobicity to the CNCs to ensure the absorption at the oil-water interface but also formed quadruple hydrogen bonding to further enhance the emulsion stability and assist the formation of microporous hydrogels.

In addition to emulsion polymerizations, grafted CNCs could also be used to generate stimuli-responsive Pickering emulsions. Thermal responsive polymers with LCST such as PNIPAM,[137] poly[2-isopropoxy-2-oxo-1,3,2-dioxaphospholane] (PIPP),[144] POEGMA,[145] pH-responsive polymers with reversible protonation and deprotonation processes like poly(methacrylic acid) (PMAA),[145] CO_2-responsive polymers such as poly(N-3-(dimethylamino) propyl methacrylamide) (PDMAPMAm)[139] and poly(N,N-(diethylamino)ethyl methacrylate) (PDEAEMA),[139] and dual responsive polymers like PDMAEMA[138] were used for modifying CNCs.

Figure 6. Schematic representation of the preparation of hollow SiO_2 microspheres with thiol-rich surfaces by Pickering emulsion directing sol-gel process. Reproduced with permission from Elsevier B.V. (ref. 131), Copyright (2020).

The styrene-in-water emulsions stabilized by CNC-*g*-P(DMAPMAm-*co*-S) or CNC-*g*-P(DEAEMA-*co*-S) were CO_2 responsive, where the pH was reversibly tuned by purging N_2 or CO_2.[139] The macroalkoxyamines could be protonated upon purging CO_2 and deprotonated upon purging N_2 so that the hydrophobicity of the polymer graft could be tuned for on-demand demulsification. PNIPAM is widely known for its LCST in the aqueous phase. Rojas *et al*. synthesized PNIPAM-*g*-CNC, where the PNIPAM brushes screened the electrostatic repulsions between CNCs.[137] Despite the hydrophilicity of PNIPAM brushes, they can still be used to impart CNCs with interfacial activities, since the isopropyl groups have a higher affinity to the oil phase. The PNIPAM-*g*-CNC was used to stabilize heptane-in-water emulsion, which could be demulsified upon heating due to the aggregation of the grafted CNCs. Iwasaki *et al*. modified the CNCs with PIPP (CNC-*g*-PIPP).[144] Polyphosphoester, another candidate with good performance in biocompatibility and biodegradability, has also been used as an LCST trigger. The modified CNCs have higher interfacial activity due to the hydrophobicity imparted with the PIPP brushes. The CNC-*g*-PIPP was used to stabilize heptane-in-water Pickering emulsion, where the demulsification could be triggered when the emulsion was heated above LCST of PIPP. Tam *et al*. synthesized PDMAEMA grafted CNCs (PDMAEMA-*g*-CNC), where PDMAEMA imparted the CNCs with both thermal and pH responsiveness.[138] O/w Pickering emulsions with toluene or heptane as the oil phase could be stabilized with deprotonated PDMAEMA chains. Demulsification could be triggered when PDMAEMA chains were protonated at decreasing pH or underwent coil-globule transition above its LCST. Tam *et al*. also synthesized grafted CNCs with binary brushes of POEGMA and PMAA (CNC-POEGMA-PMAA), which could stabilize heptane-in-water Pickering emulsions at low temperature and high pH.[145] The POEGMA brushes imparted thermal responsiveness to the emulsions, where the hydrogen bonds between the ether and water was disrupted at elevated temperature, thus the grafted CNCs will associate, triggering demulsification. The PMAA imparted pH responsiveness, where the carboxyl groups of MAA were protonated at decreased pH, formed hydrogen bonding with ethylene glycol and triggered the aggregation of grafted CNCs thus demulsification, as shown in **Fig. 7**.

Compared to chemically grafting polymer brushes on CNCs, physical absorption is less time-consuming and more environmentally friendly. Cranston *et al*. mixed CNCs with different water-soluble polymers, such as hydroxyethylcellulose (HEC) or methylcellulose (MC), so that the polymers could absorb onto the CNCs.[135] Synergistic stabilization was observed when the polymer-absorbed CNCs were used to stabilize dodecane-in-water Pickering emulsions, which means the emulsion droplets are smaller and the stability of the emulsion is higher with the polymer-absorbed CNCs than either of the components alone at the same concentration. Furthermore, MC could be used as a thickening agent to give gel-like structured emulsion upon heating above its cloud point. Cranston *et al*. also discovered that with the addition of tannic acid, the oil phase could be freeze-dried to give corn oil powder and redispersed into an emulsion by shaking, indicating that complexation between tannic acid and the polymer absorbed CNCs protected the oil droplets from coalescence even when the aqueous phase is dried.[136] This opened possibilities for food, cosmetic, and pharmaceutical-related applications where drying the o/w emulsions is required.

Compared with covalent bonds, graft copolymers could be prepared through dynamic bonds which could easily be cleaved by external stimuli. Cheng and Gao *et al*. synthesized poly[(N,N-dimethyl acrylamide)-*statistical*-(3-acrylamidophenylboronic acid)] (PDMA-*stat*-PAPBA) copolymers and PS with *cis*-diol terminals ($PS(OH)_2$) separately.[146] The hydrophilic PDMA-*stat*-PAPBA and the hydrophobic $PS(OH)_2$ could assemble at the toluene-water interface through B-O bonds and stabilize the o/w emulsions. The B-O bonds linking the backbone and the sidechains could be cleaved by external triggers, such as decreasing pH or the addition of glucose, as shown in **Fig. 8**.

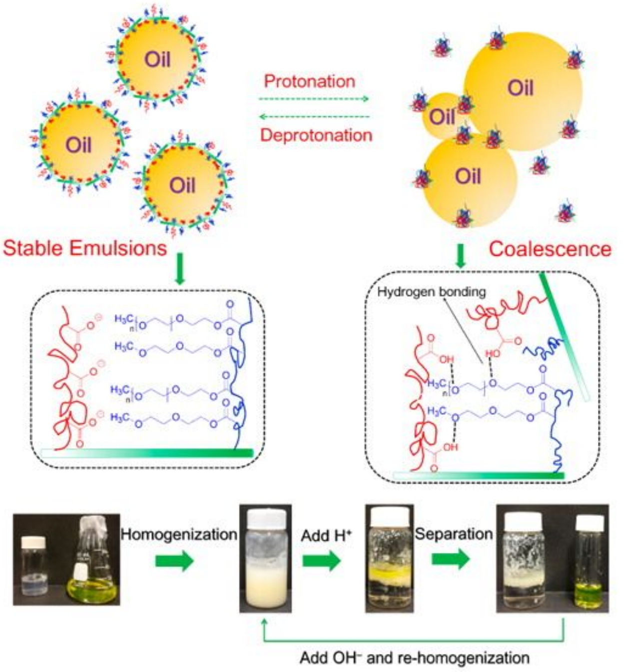


Figure 7. Schematic representation of the pH-responsive Pickering emulsions stabilized by CNC-POEGMA-PMAA. Reproduced with permission from American Chemical Society (ref. 145), Copyright (2016).

Graft copolymers could be prepared by supramolecular chemistry, where different polymer chains were connected through noncovalent bonds, like host-guest interactions. Combining the host-guest inclusion interaction and dynamic C=N bonds, Cheng and Gao *et al*. developed an amphiphilic graft copolymer with two types of dynamic processes. Poly(methyl methacrylate)-*block*-poly(((4-adamantaneimino)methyl)phenyl methacrylate) (PMMA-*b*-PAMPMA) was used as a hydrophobic backbone, where the adamantane groups could be used for host-guest inclusion interaction with β-CD terminated hydrophilic PNIPAM (PNIPAM-β-CD) to give supramolecular graft copolymers.[147] The xylene-in-water Pickering emulsion stabilized by the graft copolymer core-shell particles could be broken with the temperature increased above LCST of PNIAM or the addition of HCl to cleave the C=N linkage.

2.5 Bottlebrush polymers

Graft copolymers are generally prepared with "grafting to" or "grafting from" methods where the steric hindrance limited the grafting density of side chains. Compared with graft copolymers, bottlebrush copolymers have a high grafting density. In most cases, at least one side chain is grafted to each repeating unit. "Grafting through" method is widely used to ensure the high grafting density. The steric hindrance introduced by densely packed brushes forces the polymer backbone to extend and reduce entanglement. Compared with linear diblock copolymers, amphiphilic bottlebrush copolymers have a stronger affinity at the oil-water interface.

Verduzco *et al*. synthesized thermal responsive bottlebrush copolymers with PNIPAM as the brushes.[148] Although both the bottlebrush polymers and linear PNIPAM homopolymers can lower the interfacial energy between chloroform and water by one order of magnitude, stable emulsions could only be obtained with the linear homopolymers, indicating the inability of the bottlebrush copolymer to stabilize highly curved interface. Compared with uniformly grafted bottlebrush polymers, amphiphilic heterografted bottlebrush copolymers gave higher emulsification efficiencies. Matyjaszewski *et al*. synthesized heterografted bottlebrush copolymers with hydrophilic PEO brushes and hydrophobic PBA brushes.[71] The bottlebrush copolymers gave stable w/o emulsions (xylene or cyclohexane as the oil phase) with enhanced adsorption compared to their linear diblock copolymer analogs, as shown in **Fig. 9**. It was shown that increasing number fraction or length of the hydrophilic grafts or decreasing the solubility of the hydrophilic grafts in the oil phase imparted a higher affinity of the bottlebrush copolymers to the aqueous phase and higher emulsification efficiency. Star-like polymers with shorter backbone could stabilize larger interfacial area compared with bottlebrush copolymers due to lower structural compactness. Tilton *et al*. used interfacial dilatational rheology to study the PEO/PBA heterografted bottlebrush copolymers at xylene-water interface and found that increased hydrophilicity with longer PEO arms leads to increased modulus, non-hysteretic stress-strain response, and enhanced emulsification efficiency.[97]

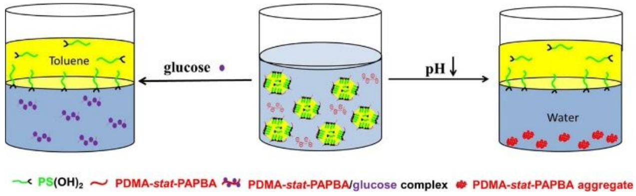


Figure 8. Schematic representation of the responsive o/w emulsion stabilized by amphiphilic PDMA-*stat*-PAPBA-*g*-PS supramolecular graft copolymers. Reproduced with permission from American Chemical Society (ref. 146), Copyright (2018).

Double-brush copolymers refer to a particular category of bottlebrush copolymers, where two different brushes are connected to each repeating unit of the polymer backbone. Double brush copolymers are usually synthesized with the "grafting through" method, where diblock copolymers with a polymerizable group at the junction point of the two blocks acted as macromonomers. Compared with statistical bottlebrush copolymers with two brushes randomly connected to the backbone, double-brush copolymers enabled precise control of the stoichiometric ratio between the two brushes and their uniform distribution along the backbone, which favored the formation of well-defined Janus conformations.

Cheng *et al*. synthesized double-brush copolymers from a macromonomer with PS and PLA as the two brushes and *exo*-norbornene groups at the block junctions.[149] The Janus conformation of the double-brush copolymers was successfully visualized with TEM and atomic force microscopy (AFM). The same group also synthesized double-brush copolymers from diblock copolymer macromonomers containing hydrophilic PEO blocks, hydrophobic PLA blocks, and *exo*-norbornene junctions.[150] Compared with the diblock copolymer macromonomers, the double-brush copolymers protected the o/w emulsions (toluene as the major component of the oil phase and hexadecane as the hydrophobe) against coalescence due to their restricted diffusion in the continuous aqueous phase. Cheng *et al*. also synthesized double-brush copolymers containing PEO and PS as the two brushes and additional RAFT active sites at the end of PS chains.[151] The styrene-in-water emulsions stabilized by the double-brush copolymers could be used for RAFT polymerization, where the double-brush copolymers served not only as surfactants but also as RAFT agents to polymerize styrene, yielding polymer latexes. With divinylbenzene present as a crosslinker, vesicular polymer nanoparticles were obtained from cross-linking polymerization.

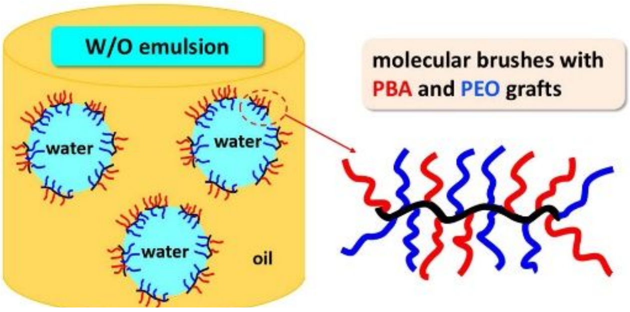


Figure 9. Schematic representation of w/o emulsion stabilized with heterografted bottlebrush copolymers. Reproduced with permission from American Chemical Society (ref. 71), Copyright (2017).

Grafting through polymerization usually suffers a low concentration of the polymerizable groups and a strong steric hindrance, thus poorly controlled M_w. When the macromonomers form core-shell micelles, the polymerizable groups could be concentrated at the boundary of the core-shell micelles, promoting intra-micelle polymerization. Furthermore, when the core-shell micelles formed Janus conformations at the oil-water interface with the core and shell extending into oil and aqueous phases separately, the polymerizable groups become even more exposed, enabling inter-micelle polymerization to higher M_w. Gao *et al*. prepared poly(methyl methacrylate)-*block*-poly(N,N-dimethyl acrylamide) (PMMA-*b*-PDMA) diblock macromonomers that had a methacryloyl group at the junction of the two blocks for grafting through polymerization.[152] The diblock macromonomer could first form micelles in the aqueous phase, then stabilize o/w Pickering emulsions (a mixture of *n*-decanol and toluene as the oil phase) with the hydrophobic cores and hydrophilic shells extending into oil and aqueous phases and the methacryloyl groups residing at the boundary, as shown in **Fig. 10**. With the mobility of the core improved with a co-solvent, the polymerization at the oil-water interface gave high molecular weights since the Janus conformation of the micelles that formed at the interface helped to overcome the hindrance from the micelle shells and enabled inter-micelle propagation. In another case, for the micelle-assisted grafting-through strategy developed by Gao *et al*., the polymerizable vinyl groups were placed at the end of the PDMA block of PDMA-*b*-PNIPAM diblock copolymers.[153] The diblock macromonomers first formed core-shell micelles at elevated temperature, followed by radical polymerization, which only proceeded within every single micelle, due to the hindrance produced by looped PDMA blocks. The prepared core-shell bottlebrush copolymers with diblock copolymers as the brushes stabilized thermal-responsive toluene-in-water emulsions, which could be demulsified upon heating above the LCST of the PNIPAM.

Instead of being used as polymer emulsifiers, bottlebrush polymers with interfacial activity can also be used as a template to prepare composite emulsifiers. Yang *et al*. synthesized poly(ethylene oxide)-*block*-poly(2-methacryloyloxyethyl pentynoate-*graft*-poly(acrylic acid))-*block*-polystyrene (PEO-*b*-P(MAPA-*g*-PAA)-*b*-PS), where the middle bottlebrush block was converted into composite nanorods, that stand vertically at the oil-water interface, due to the amphiphilicity imparted by the PEO and PS linear polymers on two ends.[154] Magnetic responsive emulsions were obtained with polymer/Ni composite Janus nanorods.

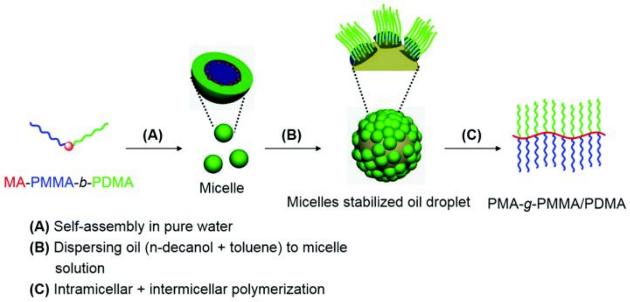


Figure 10. Schematic representation of the synthetic route of PMA-*g*-PMMA/PDMA double-brush copolymers through o/w Pickering emulsions with inter-micelle propagation. Reproduced with permission from Royal Society of Chemistry (ref. 152), Copyright (2016).

3. Conclusion and perspective

The developments in synthesis have enabled the preparation of polymers with advanced branched architectures. In comparison to their linear analogs, polymers with advanced architectures have several advantages, including higher emulsification efficiency, higher emulsion stability against coalescence, greater versatilities for on-demand demulsification, inter-droplet interactions, encapsulation for catalytic and delivery related applications, acting as both emulsifiers and macroinitiators for polymerization reactions, and compatibilization for gels. This review summarizes some of the developments in the past decade using polymers with advanced architectures as conventional amphiphilic emulsifiers, A-B-A type Gemini emulsifiers, and Pickering emulsifiers, including polymersomes assembled with block copolymers, branched polymers with multiple branching points, star polymers with well-defined small molecule or cross-linked polymer cores and uniform or mixed arms, graft copolymers with binary or tertiary grafts of varying grafting density on both flexible polymer backbones and rigid CNCs, and bottlebrush copolymers with densely packed side chains. Dynamically cleavable covalent bonds, supramolecular interactions like host-guest interaction, together with other properties of polymers like LCST and pH-depending protonation of polyelectrolytes, were applied to design stimuli-responsive polymers, where on-demand demulsification could be achieved with temperature, pH, CO_2, potential field, or the addition of certain chemicals. The versatility of polymers opens possibilities for multi-functional emulsifiers. Despite some studies about the effects of the composition of branched, star, and bottlebrush copolymers on the emulsification properties,[71,105,123] the relationship between the chemical composition of the polymers and the emulsification properties remains mostly unknown. The detailed conformations adopted by each polymer chain has a direct impact on the interfacial area covered by emulsifiers and the interfacial energy, thus the protection of dispersed droplets against coalescence. However, current studies relied more on macroscopic properties obtained from tensiometry, dynamic light scattering, and microscopy. Details about the kinetics of the absorption of polymers at the oil-water interface and the conformational evolution of the polymer chains during absorption have yet to be understood. Detailed studies of the relationship between the composition of polymer emulsifiers and the emulsification behavior and a deeper understanding of the molecular conformation at the oil-water interface will guide emulsifier design in the future.

The polymer emulsifiers with advanced architectures might even be able to lock in the non-equilibrium interfacial shape, thus break the boundary between the studies regarding emulsions and reconfigurable liquid-liquid interfaces for a broader range of applications, like 3D printing.[155] Polymers with particulate assemblies, like nanoparticles and nanorods, will also open the possibility for water-in-water emulsions.[156-158] Completely unexplored is the possibility of patterning the surface of droplets using Janus-type star copolymers or bottlebrush copolymers. Non-favorable interactions between the oil-soluble portions and water-soluble portions of the Janus-type stars will lead to a 2D phase separation that can be kinetically trapped, yielding surface morphologies ranging from bicontinuous spinodal morphologies to patchy surfaces obtained by coarsening processes and to Janus-type striped surfaces. In addition to their use as emulsifiers, star polymers, like polymer grafted nanoparticles,[159] also have potential to be used as compatibilizers for immiscible polymer blends. Bottlebrush block copolymers comprising two hydrophobic-hydrophilic bottlebrush-random-copolymer blocks, like (A-*random*-B)-*block*-(A-*random*-C), where A is hydrophilic brush while B and C are immiscible hydrophobic brushes, can be used as emulsifiers at the oil-water interface. Surface morphological characteristic mimicking linear diblock copolymers will be achieved, having all the classic morphologies but in 2D. The size of the heterogeneities at the interface will be dictated by the lengths of the blocks in the bottlebrush copolymer. In all cases, the interface can be responsive to applied external forces and external stimuli.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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