

# Supramolecular Polymer Emulsifiers for One-step Complex Emulsions

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**Abstract** Complex emulsions, such as double emulsions and high-internal-phase emulsions, have shown great applications in the fields of drug delivery, sensing, catalysis, oil-water separation and self-healing materials. Their controllable preparation is at the forefront of interface and material science. Surfactants and polymers have been widely used as emulsifiers for building complex emulsions. Yet some inherent disadvantages exist including multi-step emulsifications and low production efficiency. Alternatively, supramolecular polymer emulsifier for complex emulsions *via* one-step emulsification is rising as a new strategy due to the ease of preparation. In this feature article, we review our recent progresses in using supramolecular polymer emulsifiers for the preparation of complex emulsions. Double emulsions and high-internal-phase emulsions are successfully prepared *via* one-step emulsification with the help of different supramolecular interactions including electrostatic, hydrogen bond, coordination interaction and dynamic covalent bond, which will be particularly emphasized in detail. In the end, a comprehensive prospect is given for the future development of this field. This article is expected to provide new inspirations for preparing complex emulsions *via* supramolecular routes.

**Keywords** Complex emulsions; Double emulsions; High-internal-phase emulsions; Supramolecular interaction; One-step emulsification

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## INTRODUCTION

Emulsions have attracted extensive attentions in many areas such as cosmetic, food industry, agricultural agents, petrochemical, and materials engineering<sup>[1–18]</sup>. In recent years, a tremendous increase of effort has been especially paid to the preparation of complex emulsions including double emulsions and high-internal-phase emulsions (HIPEs). These complex emulsions are particularly used as soft templates to fabricate functional porous materials which have shown extraordinary potentials and advantages in drug delivery, sensing, catalysis, oil-water separation and self-healing materials<sup>[19–33]</sup>. However, as multiphase mixture systems, complex emulsions are in essence thermodynamically unstable, subject to the uncontrollable droplet coalescence and phase separation. To maintain their long-term stability, interfacially active emulsifiers are essentially needed in order to isolate the heterogeneous phases *via* multiple interfaces. Although small molecular surfactants have been developed as extensively used emulsifiers to build complex emulsions, they are encountering some inherent problems including low production efficiency, excessive use, difficult removal, and potential cytotoxicity issues<sup>[34–36]</sup>. There is an increasing demand for novel emulsifiers to prepare complex emulsions *via* highly convenient and economical ways.

Amphiphilic polymers are rising as an intriguing class of interfacially active materials for preparing complex emulsions in consideration of the improved biocompatibility and interfacial stability<sup>[37–41]</sup>. Compared with small molecular surfactants to serve as the emulsifiers, the amphiphilic polymers can efficiently aggregate at oil/water interfaces and assemble into a denser molecular layer, which provides a more robust barrier against droplet coalescence and thus increases the stability of complex emulsions. In addition, the precise regulation of polymer emulsifying performance by tailoring the polymer compositions also affords great promise to control the emulsion morphologies and types<sup>[42–47]</sup>. However, the process to prepare the ideal polymers with elegant topologies and appropriate emulsifying performance always relies on cost-ineffective synthesis and laborious separation trials, which likely restricts the application of polymers in manufacturing complex emulsions and derived materials.

In the past several years, our group has devoted great effort to developing a new strategy of preparing complex emulsions based on supramolecular polymer emulsifiers, aiming to save time and effort in the process of exploiting polymeric emulsifiers with ideal emulsifying performance. In this paper, several examples of double emulsions and high-internal-phase emulsions, which are stabilized by supramolecular polymer emulsifiers and readily prepared *via* one-step emulsification, will be specifically highlighted. In order to tailor the emulsifying performance of the polymer emulsifiers, different types of supramolecular interactions are used, including electrostatic interaction, hydrogen bond,

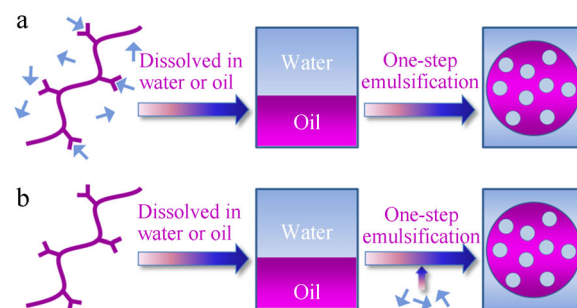
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coordination interaction and dynamic covalent bond. This feature article is expected to stimulate interests in preparing complex emulsions *via* supramolecular routes, and make contributions to extending the research scope of complex emulsions and their future applications in many fields.

## ONE-STEP DOUBLE EMULSIONS

Double emulsion, such as water-in-oil-in-water (W/O/W) emulsion or oil-in-water-in-oil (O/W/O) emulsion, is an artful dispersive system consisting of three separated phases, which has attracted enormous attention as soft templates for porous materials and in loading immiscible excipients<sup>[3, 48–54]</sup>. Many endeavors have been made in developing the preparation methods for double emulsions<sup>[38, 39, 55–64]</sup>. Among them, one-step emulsification method using supramolecular polymer emulsifiers comes into focus due to the ease of operation and low cost<sup>[37, 65–70]</sup>. In general, the oil-water binary mixtures are directly emulsified into double emulsions *via* one-step emulsification. Polymers are used in this method, dissolved in water or oil phase as emulsifiers. Different from the common polymeric emulsifiers with given emulsifying performance, supramolecular polymer emulsifiers possess variable interfacial activities relying on their tunable supramolecular compositions. As such, several emulsion types can be achieved in one polymer system. The method for preparing one-step double emulsions involves two specific pathways as shown in Scheme 1: one is to dissolve the prepared supramolecular polymer emulsifiers in water or oil phases followed by emulsification and the other one is to turn the polymers into supramolecular emulsifiers after mixing the water and oil phases. The key difference between them lies in the period when supramolecular polymer emulsifiers are formed.

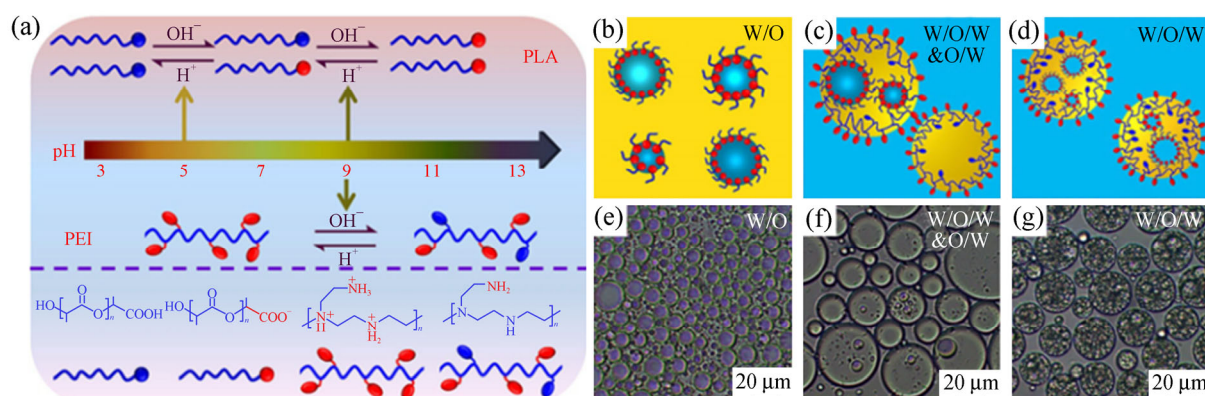
Several examples using supramolecular polymer emulsifiers for one-step double emulsions have been presented in our recent studies. For example, a W/O/W double emulsion with long-term stability was successfully prepared *via* one-step emulsification based on the cooperation of the polylactic acid (PLA) and polyethyleneimine (PEI)<sup>[71]</sup>.



**Scheme 1** Schematic illustration of the preparation processes of one-step double emulsions using supramolecular polymer emulsifiers prepared (a) before and (b) after mixing the oil and water phases

pH condition of aqueous solution can change the protonation states of PLA and PEI through electrostatic interaction, which has a great effect on their emulsifying performances and the obtained emulsion types. As shown in Fig. 1(a), the terminal carboxyl group of PLA can be deprotonated at pH values above its  $pK_a$  (3.5–5.0). When dissolved in dichloromethane, it is considered as an oil-soluble emulsifier to stabilize the W/O interface. PEI with higher  $pK_a$  (9.5–11) is interfacially inactive at low pH due to full protonation. Once pH reaches above its  $pK_a$ , PEI behaves like a water-soluble emulsifier to stabilize the O/W interface. As a result, macroscopic phase separation occurs because of the absence of interfacial stabilizers at acidic condition (pH = 3–5). At pH = 7, W/O emulsions are obtained because only PLA plays a role at W/O interfaces (Fig. 1e). When the aqueous solution becomes slightly basic (pH ~9), O/W emulsions surrounded with a few W/O/W emulsions are observed (Fig. 1f), indicating that PEI also becomes active at the interfaces. Further increase of the pH value leads to W/O/W double emulsions with more internal phase (Fig. 1g). The synergistic effect of these two polymers is responsible for the formation of stable W/O/W double emulsion at high pH value.

It was found that without the assistance of PEI, PLA can also facilitate the formation of double emulsions through changing the pH conditions. An emulsion system consisting

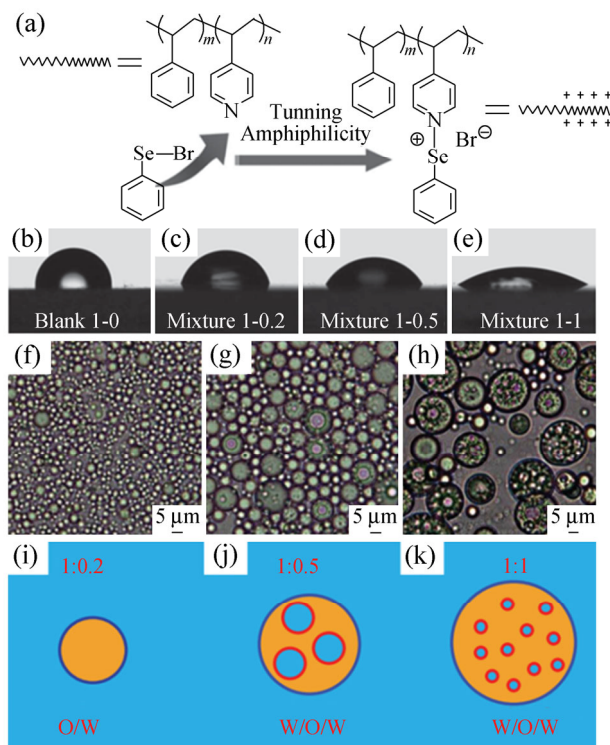


**Fig. 1** (a) Tailoring the emulsifying performance of polymers and corresponding emulsion types by changing pH values and possible protonation states of PLA and PEI at different pH values; Schematic illustration and bright-field microscopy images of emulsions at different pH values: (b, e) W/O single emulsions at pH = 7, (c, f) O/W or W/O/W double emulsions at pH = 9, (d, g) W/O/W double emulsions at pH = 11–13 (Adapted with permission from Ref. [71]; Copyright (2017) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany)

of PLA dichloromethane solution as an oil phase and bovine serum albumin (BSA) aqueous solution was investigated<sup>[72, 73]</sup>. Single O/W emulsions were observed at acidic conditions, while W/O/W double emulsions were prepared at basic conditions because PLA becomes amphiphilic when the terminal carboxyl group of PLA is deprotonated. Associating PLA with cationic small molecules plays a similar role to changing the protonation states of PLA in building double emulsions comprised of PLA. Double emulsions were formed when a dichloromethane solution containing PLA was emulsified into an aqueous solution containing cetyltrimethyl ammonium bromide (CTAB)<sup>[74]</sup>. However, when poly(vinyl alcohol) (PVA) or sodium dodecyl sulphate (SDS) was used instead of CTAB, almost no double emulsion was observed. A weak electrostatic interaction is assumed to exist between the carboxylic group of PLA and the cationic moiety of CTAB, which disturbs the oil/water interface and leads to an introduction of external water phase into the internal, thus forming random aqueous beads in oil droplets. However, PVA is a nonionic surfactant and SDS is an anionic surfactant. In these cases, the interaction of PLA with PVA or SDS is relatively weak, which hinders the formation of double emulsions.

Another one-step emulsion system was also developed based on a block copolymer, poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP)<sup>[75]</sup>. The unmodified block copolymer is hydrophobic due to the hydrophobic nature of PS and P4VP segments, as determined by a water contact angle of more than 90° (Fig. 2b). When it is used as an emulsifier, macroscopic phase separation occurs immediately once homogenization stops. The emulsifying performance of this polymer can be tuned upon the formation of supramolecular complexes with a selenium-containing small molecule *via* Se–N dynamic covalent bond, as shown in Fig. 2(a). The formation of Se–N covalent bond further generates the N–Se cation and the bromide counterion, which imparts the hydrophilic property to the P4VP segment and endows this polymer with interfacial activity. A decrease in the water contact angles confirms the formation of supramolecular complexes (Figs. 2c–2e). Different emulsions were acquired after one-step emulsification using these supramolecular polymer emulsifiers (Figs. 2f–2k). When the emulsifying performance of this polymer was appropriately improved (Figs. 2g and 2j), W/O/W double emulsions containing one or several internal water droplets were obtained. A better emulsifying performance produced more remarkable W/O/W double emulsions with more internal water droplets (Figs. 2h and 2k). The emulsifying performance as well as the interfacial activity of polymer can also manipulate the emulsion morphologies by controlling the phase separation process *via* a supramolecular route, which has been demonstrated in an emulsion system consisting of P4VP-oleic acid<sup>[76]</sup>.

The concept of supramolecular polymer emulsifier for complex emulsions has proved to be feasible and facile in building one-step double emulsions by the emulsion systems above. But only using one simple homopolymer as an emulsifier is still challenging. Recently, a commonly used homopolymer, poly(ethylene glycol) (PEG), was successfully explored as emulsifiers to prepare double emulsions *via*

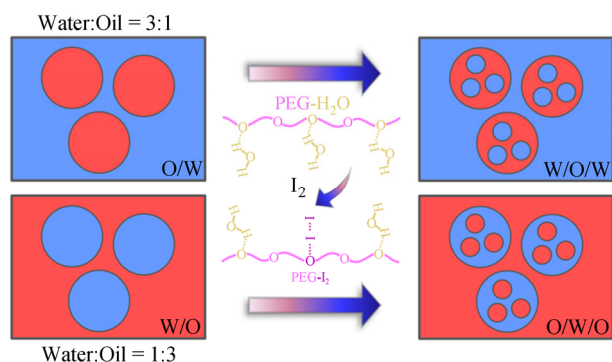


**Fig. 2** (a) Schematic illustration of the formation of supramolecular emulsifiers between PS-*b*-P4VP and PhSeBr *via* Se–N dynamic covalent bond; (b–e) Contact angles of supramolecular emulsifiers at different molar ratios between the pyridine group and PhSeBr of (b) 1:0, (c) 1:0.2, (d) 1:0.5, and (e) 1:1; (f–k) Bright-field microscopy images and schematics of emulsions prepared at different molar ratios: (f, i) 1:0.2, (g, j) 1:0.5, and (h, k) 1:1 (Adapted with permission from Ref. [75]; Copyright (2014) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany)

one-step emulsification<sup>[77]</sup>. It was found that the ether groups of PEG can interact with water molecules *via* hydrogen bond interaction to form a supramolecular complex termed PEG-H<sub>2</sub>O. The PEG-H<sub>2</sub>O complex exhibits amphiphilic performance to stabilize oil/water interfaces. In a water-chloroform binary system, single emulsions (O/W or W/O) or double W/O/W emulsions can be obtained with the appropriate use of oil-water ratio and PEG concentration. The emulsifying performance of PEG was further tailored by associating it with iodine to form another supramolecular complex PEG-I<sub>2</sub> through coordination interaction, which leads to an enhanced lipophilicity. This alteration of emulsifying performance induces the conversion from single emulsions to double emulsions, as summarized in Fig. 3. Water or iodine behaves as a critical supramolecular actuator to manipulate the emulsifying performance of PEG, which enables the phase inversion from simple emulsions to complex emulsions.

## ONE-STEP HIGH-INTERNAL-PHASE EMULSIONS

In general emulsions such as single or double emulsions, the dispersed phase exists in continuous phase in a form of noncontiguous spherical droplets. Once the volume fraction



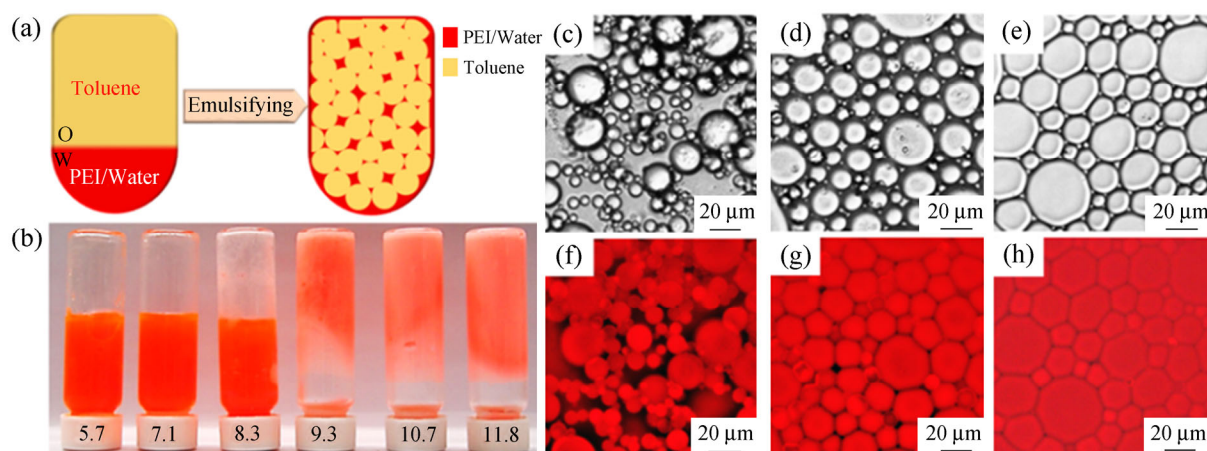
**Fig. 3** Schematic illustration of the preparation of one-step double emulsions using PEG-H<sub>2</sub>O or PEG-I<sub>2</sub> complexes as emulsifiers (Reprinted with permission from Ref. [77]; Copyright (2017) American Chemical Society)

of the dispersed phase increases to 74.05% or more, spherical emulsion droplets deform into polyhedra with broad polydispersity and take a form of close packing due to overcrowding<sup>[78–80]</sup>. Thus emulsions with extraordinarily high internal-phase volume are attained and termed high-internal-phase emulsions (HIPEs). In terms of emulsion morphologies, high-internal-phase emulsions are generally classified into two categories: O/W and W/O type emulsions, which is similar to that of single emulsions. However, the unique oil/water complex structure makes high-internal-phase emulsions different from the single emulsions and also rank as one of complex emulsions. Although the high-internal-phase emulsions are also prepared *via* one-step emulsification with the use of emulsifiers, the structural feature makes high demands of the emulsifiers for interfacial activity and stability, not only facilitating the formation of the polyhedral cells, but also maintaining the emulsion stability and avoiding droplet coalescence and phase separation. The dynamic stabilization of small-molecule surfactants is intrinsically insufficient, and if applied to the preparation of HIPEs, a significant amount is required, for example at least 5 wt%, and typically 20 wt%<sup>[81–84]</sup>. Solid particle is another commonly used emulsifier for HIPEs, but their limited interfacial activity leads to the maximum internal-phase

volume in theory and experiment below 70%, unless the geometry and dimension of particles are well regulated and their surface is deliberately modified<sup>[85–95]</sup>. Polymeric emulsifiers have been also used as an alternative, but are still at an infancy stage<sup>[40, 41, 96–104]</sup>. As part of an ongoing study, the strategy of supramolecular polymer emulsifiers for complex emulsions is extended to the preparation of one-step HIPEs, which has proved to be efficient in our recent work.

As stated in the above section, the interfacial performance of PEI can be changed through electrostatic interaction. When used as emulsifiers in combination with PLA, double emulsions can be obtained in the basic conditions. Different emulsion morphology was observed when only PEI was intended as emulsifiers<sup>[105]</sup>. As illustrated in Fig. 4(a), an aqueous solution containing PEI was emulsified into toluene with an oil-water ratio of 4:1 to form an emulsion under vigorous agitation. Far from a normal W/O emulsion, an O/W HIPE was formed, in which the internal-phase volume was estimated to be about 80%. The pH value of aqueous solution has great influence on the phase behaviors of emulsions (Fig. 4b). HIPE cannot be formed in acidic conditions and slightly basic environment is not enough to facilitate the formation of stable HIPEs. At pH of 8.3, an O/W emulsion was obtained but relatively unstable (Figs. 4c and 4f). HIPE was obtained once the pH value was changed to 9.3 (Figs. 4d and 4g). The emulsion morphology can be maintained for 48 h, and a partial phase separation occurred after that. When pH value was increased to 11.8, a stable HIPE was formed (Figs. 4e and 4h). It is believed that the improved emulsifying performance as a result of the deprotonation of PEI at high pH values should be responsible for the formation and stability of HIPEs. In addition, it was found that self-assembly of PEI in the aqueous solution also made contributions to the formation of HIPEs. Compared with free PEI molecules, the self-assembled nano-aggregates possess better interfacial activity because of Pickering effect which refers to that nanoparticles can decrease the interfacial energy more efficiently.

Another system based on PS-*b*-P4VP in previous work is also developed for one-step HIPEs<sup>[106]</sup>. Instead of



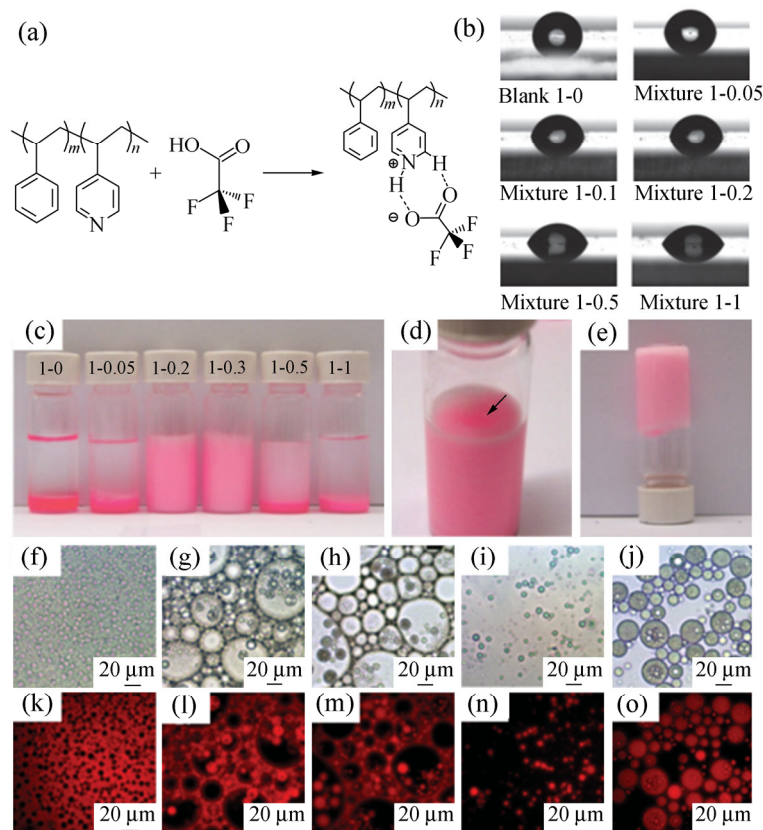
**Fig. 4** (a) Schematic illustration of the preparation process of one-step emulsions; (b) Optical images of PEI HIPEs prepared at different pH values; (f–h) Bright-field and fluorescence microscopy images of emulsions prepared at different pH values: (c, f) pH = 8.3; (d, g) pH = 9.3; (e, h) pH = 11.8 (Adapted with permission from [105]; Copyright (2017) American Chemical Society)

selenium-containing small molecule, trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ ) is selected to form supramolecular polymer emulsifiers with PS-*b*-P4VP *via* hydrogen bond interaction as shown in Fig. 5(a), which is expected to extend the adjustable scope of emulsifying performance of PS-*b*-P4VP and facilitate the formation of HIPEs. As characterized by the water contact angle in Fig. 5(b), this block copolymer is hydrophobic. When the pristine hydrophobic PS-*b*-P4VP was used as emulsifiers in a water-dichloromethane binary system with a water-oil ratio of 5:1, macroscopic phase separation occurred immediately once emulsification stopped (Fig. 5c). After interacting with  $\text{CF}_3\text{COOH}$ , a decrease in the water contact angle is observed due to hydrophilization of the P4VP segment, which suggests the improved emulsifying performance of this block copolymer. When a small amount of  $\text{CF}_3\text{COOH}$  was added, a W/O emulsion was formed because the emulsifying performance of this block copolymer was only slightly changed and the quite hydrophobic skeleton still favored the formation of W/O emulsions (Figs. 5f and 5k). Using a largely improved supramolecular polymer emulsifiers results in an O/W emulsion (Figs. 5i and 5n) and a W/O/W double emulsion (Figs. 5j and 5o), similar to our previous work. A W/O HIPE was obtained when the emulsifying performance of the polymer was appropriately improved. Microscopic polyhedral structures as well as

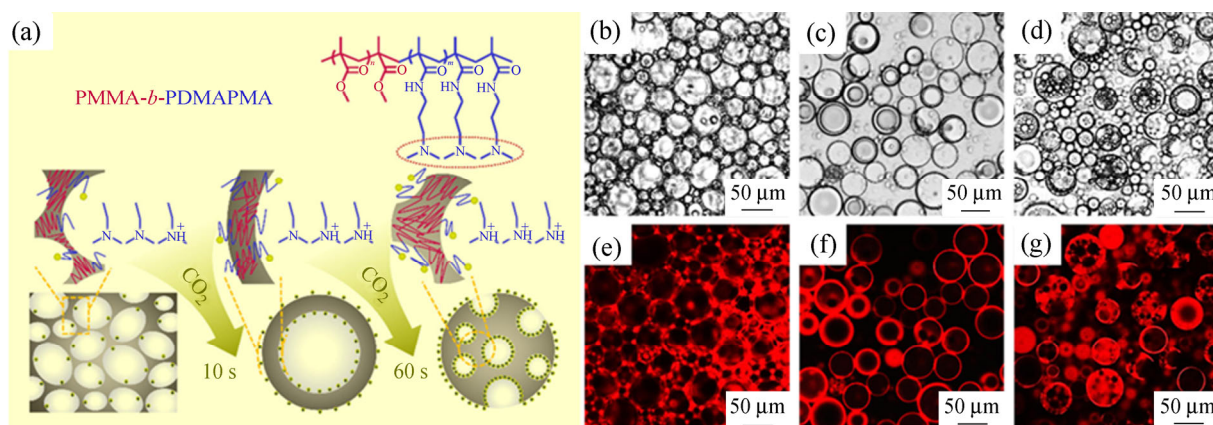
polydisperse sizes are clearly observed in Figs. 5(g), 5(l), 5(h), and 5(m). And the HIPE possessed a long-term stability more than two weeks.

## CONCLUSIONS AND PERSPECTIVES

In this feature article, the concept of supramolecular polymer emulsifiers for one-step complex emulsions was proposed in order to solve the scientific problems in the preparation of complex emulsions. With the help of multiple supramolecular interactions including electrostatic interaction, hydrogen bond, coordination interaction and dynamic covalent bond, it is proved that double emulsions and high-internal-phase emulsions have been successfully prepared *via* this excellent strategy. Compared with traditional methods for preparation of these complex emulsions, supramolecular polymer emulsifiers for one-step complex emulsions have shown powerful advantages and this line of research will open a new avenue to guide the preparation of complex emulsions *via* supramolecular routes. However, there are still existing challenges and opportunities in this field: (1) in the formation of supramolecular polymer emulsifiers, additional substances besides polymer hosts are still needed to involve in the whole emulsion system such as small molecules, acid or base, which may increase the complexity of emulsions and lead the



**Fig. 5** (a) Schematic illustration of the interaction between the PS-*b*-P4VP and  $\text{CF}_3\text{COOH}$ ; (b) Contact angles of different supramolecular emulsifiers consisting of PS-*b*-P4VP and  $\text{CF}_3\text{COOH}$ ; (c–e) Optical, (f–j) bright-field microscopy, and (k–o) fluorescence microscopy images of the emulsions prepared using different supramolecular emulsifiers, where the molar ratio of pyridine rings to carboxyl groups: 1:0, (f, k) 1:0.05, (g, l) 1:0.2, (h, m) 1:0.3, (i, n) 1:0.5, and (j, o) 1:1; (d, e) Optical images of the emulsions (1:0.2) (d) immediately after emulsification and (e) after being stored upside down for two weeks (Adapted with permission from Ref. [106]; Copyright (2015) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany)



**Fig. 6** (a) Schematic illustration of one-step preparation of double emulsions and HIPES; (b–d) Bright-field and (e–g) fluorescence microscopy images of emulsions prepared using PMMA-*b*-PDMAPMA under different CO<sub>2</sub> bubbling time: (b, e) 0 s, (c, f) 10 s, and (d, g) 60 s (Adapted with permission from Ref. [107]; Copyright (2016) American Chemical Society)

emulsions to undergo irreversible changes; (2) different types of complex emulsions are difficult to achieve in a given system, which makes it harder to establish a systematic rule to predict the emulsion morphology and type by correlating the characteristic feature of supramolecular polymer emulsifiers with their interfacial performance; (3) when the complex emulsions were used as soft templates for porous materials, the supramolecular polymer emulsifier only plays a role of an emulsifier and an additional material matrix is needed.

A recent research study should be highlighted with respect to its breakthrough in overcoming these challenges, which provides new inspirations for building complex emulsions using polymeric emulsifiers<sup>[107]</sup>. In this work, a block copolymer is designed to consist of a long hydrophobic chain of polymethylmethacrylate (PMMA) segment and a CO<sub>2</sub>-responsive poly(dimethylaminopropyl methacrylamide) (PDMAPMA) segment, in order to act as both the emulsifier and emulsion matrix in the preparation of emulsions. As shown in Fig. 6(a), the hydrophobic PMMA segment and hydrophilic PDMAPMA segment endow the block copolymer with certain emulsifying performance. Without the addition of any other surfactants, a HIPE was formed by emulsifying an oil phase containing this block copolymer into a water phase with a water-oil ratio of 5:1 *via* one-step emulsification (Figs. 6b and 6e). CO<sub>2</sub> is selected as an ideal supramolecular actuator to tailor the emulsifying performance of PMMA-*b*-PDMAPMA because it can be bubbled into aqueous solution to protonate the tertiary amine groups and easily erased by heating or purging inert gas into the system. As shown in Figs. 6(c) and 6(f), after bubbling CO<sub>2</sub> for 10 s into the water-oil system, a transition from W/O HIPE to W/O/W double emulsion occurred due to the increased hydrophilicity of the copolymer as a result of PDMAPMA protonation. An increase in the amount of CO<sub>2</sub> leads to more remarkable double emulsions. After purging CO<sub>2</sub> for 1 min, W/O/W double emulsions were still obtained and multiple water droplets were loaded in each oil droplet (Figs. 6d and 6g). The long PMMA block provides a robust mechanical performance, which enables the solidification of the complex emulsions into porous materials without the use of other filling matrix. In addition, the block copolymers can

be fully recovered to the original state once the CO<sub>2</sub> is removed and re-form specific porous materials *via* the same process again.

Inspired by this work, it is believed that the future efforts should be focused on several issues in this field: (1) based on the features of different supramolecular routes, erasable stimuli-response system should be more widely used in tailoring the emulsifying performance of polymers, for example, the electrostatic interaction systems using gases such as CO<sub>2</sub> and NO as actuators, and the hydrogen bond interaction and dynamic covalent bond systems using light irradiation such as ultraviolet or near-infrared light; (2) more emulsion systems, in which reversible phase inversion from HIPES to double emulsions can be achieved, should be exploited and investigated so that a systematic rule can be obtained in combination of computational calculation and simulation to guide the preparation of complex emulsions; (3) novel polymers should be synthesized and selected to serve as solidified matrix as well as interfacial emulsifiers, avoiding the complexity of emulsion systems and potential side effects of other emulsifiers.

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