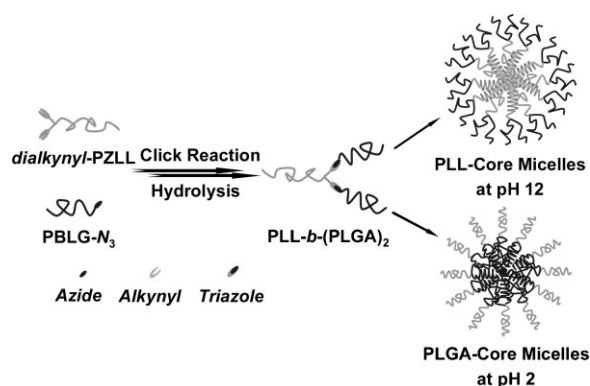


Supramolecular Self-Assembly of Nonlinear Amphiphilic and Double Hydrophilic Block Copolymers in Aqueous Solutions

Zhishen Ge, Shiyong Liu*

Supramolecular self-assembly of block copolymers in aqueous solution has received ever-increasing interest over the past few decades due to diverse biological and technological applications in drug delivery, imaging, sensing and catalysis. In addition to relative block lengths, molecular weights and solution conditions, chain architectures of block copolymers can also dramatically affect their self-assembling properties in selective solvents. This feature article mainly focuses on recent developments in the field of supramolecular self-assembly of amphiphilic and double hydrophilic block copolymers (DHBCs) possessing nonlinear chain topologies, including miktoarm star polymers, dendritic-linear block copolymers, cyclic block copolymers and comb-shaped copolymer brushes.



Introduction

It has been well established that amphiphilic block copolymers can self-assemble in aqueous solution into a variety of morphological structures including spheres, rods, lamellae, vesicles and large compound micelles or vesicles.^[1–6] Over the past few decades, this field has received ever-increasing interest due to the fact that block copolymer assemblies possess important biological or technological applications in drug delivery,^[7–9] imaging,^[10–13] sensing^[14,15] and catalysis.^[16–20] Notably, double hydrophilic block copolymers (DHBCs) represent a

special type of amphiphilic block copolymer, which can reversibly switch between micellar and unimer states depending on external conditions such as pH, temperature, ionic strength and light irradiation.^[21–25] Certain stimuli-responsive DHBCs can even exhibit a “schizophrenic” micellization character, forming two or more types of aggregates with “invertible” nanostructures upon judicious adjustment of external conditions.^[21,22,25–30] A recent surge in the field of DHBCs has further broadened the applications of block copolymer assemblies.^[31–36]

For linear amphiphilic and double hydrophilic block copolymers, previous literature reports have established that the basic structural parameters of their supramolecular assemblies in aqueous solution, including aggregate size, morphology, critical aggregation concentration (CAC) and colloidal stability, are mainly determined by relative block lengths, molecular weights (MWs) and solution conditions.^[32,33,37–41] Though it has been generally recognized that the chain architecture of block copolymers can also dramatically affect their self-assembling

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behavior,^[37,38,42,43] less has been done experimentally and theoretically to elucidate this issue.

This feature article mainly focuses on recent developments in the emerging field of supramolecular self-assembly of amphiphilic and double hydrophilic block copolymers (DHBCs) possessing nonlinear chain topologies, including miktoarm star polymers, dendritic-linear block copolymers, cyclic block copolymers and comb-shaped copolymer brushes. We will not go into further detail concerning their synthetic strategies and interested readers are encouraged to obtain this information from relevant references and several excellent review articles.^[42–47]

Amphiphilic and Double Hydrophilic Star Copolymers

Star polymers typically consist of three or more linear chains covalently or non-covalently linked to a central core. Various techniques such as high vacuum anionic polymerization,^[48,49] atom transfer radical polymerization (ATRP),^[44,47,50] reversible addition-fragmentation chain

transfer (RAFT),^[51,52] ring-opening polymerization (ROP),^[53] nitroxide-mediated radical polymerization (NMP),^[54] click chemistry^[55–57] or a combination of them^[58–63] have been successfully developed toward their synthesis. Depending on their chain topologies, amphiphilic and double hydrophilic star copolymers can be further categorized into AB_n ($n \geq 2$), A_nBA_n ($n \geq 2$) and ABC miktoarm star types.

AB₂ Miktoarm Star Copolymers

Asymmetric AB₂-type miktoarm star copolymers are also referred as “Y-shaped” block copolymers. An original example concerning the self-assembly of AB₂ miktoarm star copolymers was conducted in organic solvent, as reported by Hadjichristidis, Pispas and coworkers.^[64] They synthesized Y-shaped PS-*b*-(PI)₂ and (PS)₂-*b*-PI, and linear PS-*b*-PI block copolymers with comparable composition and overall MW via high vacuum anionic polymerization, where PS and PI represent polystyrene and polyisoprene, respectively. In *n*-decane, a selective solvent for the PI block, it was found that sizes and aggregation numbers (N_{agg}) of micelles self-assembled from these three types of block copolymers increase in the order PS-*b*-(PI)₂ < (PS)₂-*b*-PI < PS-*b*-PI. The presence of only one solvated chain in the micelle corona region has thus been proved to considerably alter micellar characteristics. They also successfully developed a scaling theory to explain the different assembling behavior of linear and nonlinear block copolymers by taking account of free energy contributions from the micellar core, corona and interfacial regions.

Concerning amphiphilic AB₂ miktoarm star copolymers, our research group reported the synthesis and self-assembly of well-defined amphiphilic PCL-*b*-(PDMA)₂ and (PCL)₂-*b*-PDMA Y-shaped miktoarm star copolymers, where PCL and PDMA are poly(ϵ -caprolactone) and poly-(2-(dimethylamino)ethyl methacrylate), respectively.^[62] Compared to linear PCL-*b*-PDMA block copolymer with similar PCL and PDMA contents, we observed that PCL-*b*-(PDMA)₂ and (PCL)₂-*b*-PDMA self-assemble in aqueous solution into spherical micelles of smaller N_{agg} , core radius (R_{core}) and intensity-average hydrodynamic radius ($\langle R_h \rangle$). Among these three types of amphiphilic block copolymers, PCL-*b*-(PDMA)₂ forms aggregates possessing the smallest N_{agg} and $\langle R_h \rangle$, and the largest overall micelle density due to the enhanced stabilization effects of two well-solvated PDMA chains per junction at the core-corona interface, which favors the bending of the core-corona interface and the formation of densely-packed core-shell nanostructures. The above results are in reasonable agreement with those obtained by Hadjichristidis et al. for block copolymers consisting of PS and PI sequences.^[64] Taton et al.^[65,66] also reported the synthesis and self-assembly of Y-shaped block copolymers consisting of hydrophobic PS and hydrophilic

poly(acrylic acid) (PAA) or poly(L-glutamic acid) (PLGA) arms. In both cases, well-defined pH-responsive spherical assemblies can form in aqueous solution.

Micellar aggregates self-assembled from amphiphilic Y-shaped miktoarm star copolymers have been explored as drug delivery nanocarriers. Guo et al.^[67] synthesized amphiphilic and biocompatible PEO-*b*-(PTMC)₂ AB₂ miktoarm star copolymers, where PEO and PTMC represent poly(ethylene oxide) and poly(trimethylene carbonate), respectively. *In vitro* studies revealed that drug release rate decreases with the increase of hydrophobic PTMC chain lengths. Thus, controlled-release properties of this novel type of drug nanocarrier can be tuned by the block compositions of Y-shaped PEO-*b*-(PTMC)₂.

The first few examples of double hydrophilic AB₂ miktoarm star copolymers were reported by Armes and coworkers.^[68–70] They prepared a wide range of pH- and thermo-responsive Y-shaped miktoarm star copolymers via the ATRP of several methacrylate monomers under mild conditions, starting from water-soluble difunctional macroinitiators. In a specific example, a Y-shaped miktoarm star copolymer of propylene oxide (PO) and 2-(diethylamino)ethyl methacrylate (DEA), PPO-*b*-(PSBMA)₂, can exhibit a thermo-induced micelle-unimer-micelle transition, taking advantage of the fact that PPO and PSBMA possess lower and upper critical solution temperature (LCST and UCST) phase behaviors in aqueous solution, respectively. They concluded that Y-shaped star copolymers exhibit considerably different aggregation properties in terms of critical micellization concentration (CMC) and micelle sizes.

The incorporation of polypeptide sequences, such as pH-responsive poly(L-lysine) (PLL) and PLGA, into DHBCs can endow them with additional structural versatility, tunable spatial arrangement of chain segments within self-assembled nanostructures, enhanced biocompatibility and broader applications in the field of biomedicines, which represents a promising new direction in the field of DHBCs. Previous literature reports mainly focused on linear purely polypeptide-based or polypeptide hybrid block copolymers.^[71,72] In two notable examples, Lecommandoux et al.^[73] reported that linear PLGA-*b*-PLL diblock copolymer can self-assemble in aqueous solution into two types of unilamellar vesicles at pH 3 and 12, respectively, by taking advantage of the formation of secondary structures and block composition asymmetry. Deming et al.^[74] synthesized non-ionic block copolypeptides of L-leucine and ethylene glycol-modified L-lysine residues, which can self-assemble into complex nanostructures such as giant vesicles, sheet-like membranes and irregular aggregates in aqueous solution. Just recently, we synthesized water-soluble AB₂ Y-shaped miktoarm star polypeptide copolymer, PLL-*b*-(PLGA)₂, via a combination of the ROP of α -amino acid *N*-carboxyanhydride (NCA) and click chemistry.^[75] Interestingly, Y-shaped PLL-*b*-(PLGA)₂ can self-assemble

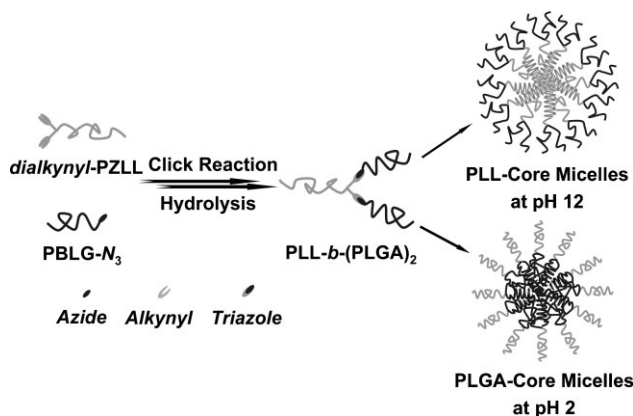


Figure 1. pH-responsive “schizophrenic” micellization of AB₂ Y-shaped miktoarm star copolymer, PLL-*b*-(PLGA)₂, in aqueous solution accompanied with coil-to-helix transitions.

into PLGA-core micelles at acidic pH and PLL-core micelles at alkaline pH, accompanied with the coil-to-helix transition of PLGA and PLL sequences (Figure 1). It is quite expected that, by varying the relative block length ratios, more robust and intriguing supramolecular assemblies can be fabricated from this novel type of purely polypeptide-based nonlinear block copolymers.

AB_n ($n \geq 2$) Miktoarm Star Copolymers

The first few examples of amphiphilic AB_n ($n > 2$) miktoarm star copolymers were exclusively synthesized via living anionic polymerization techniques and investigations concerning their self-assembly in aqueous solution were quite rare.^[48,49] Later, Tsukruk et al.^[76,77] synthesized amphiphilic PEO-*b*-PS_n by coupling living anionic polymerization and ATRP techniques. They observed that PEO-*b*-PS_n has a strong tendency to form nanostructured aggregates at the air/water interface. Recently, we reported the synthesis and “schizophrenic” self-assembly of an AB₄ miktoarm star copolymer of *N*-isopropylacrylamide (NIPAM) and DEA, PNIPAM-*b*-(PDEA)₄, consisting of thermo-responsive PNIPAM and pH-responsive PDEA arms.^[78] For comparison, PNIPAM-*b*-PDEA linear diblock copolymer with comparable MW and block composition was also prepared. Intriguingly, PNIPAM-core micelles form in acidic media at elevated temperatures, whereas structurally inverted PDEA-core micelles form in slightly alkaline conditions at room temperature (Figure 2). We further observed that the size of PDEA-core micelles self-assembled from PNIPAM-*b*-(PDEA)₄ was considerably smaller than that of linear PNIPAM-*b*-PDEA diblock copolymer. Moreover, pH-induced micellization kinetics of AB₄ miktoarm star and linear AB diblock copolymers were also investigated by the stopped-flow light scattering technique upon a pH jump from 4 to 10. Typical kinetic traces for the micellization of both types of copolymers can be fitted well

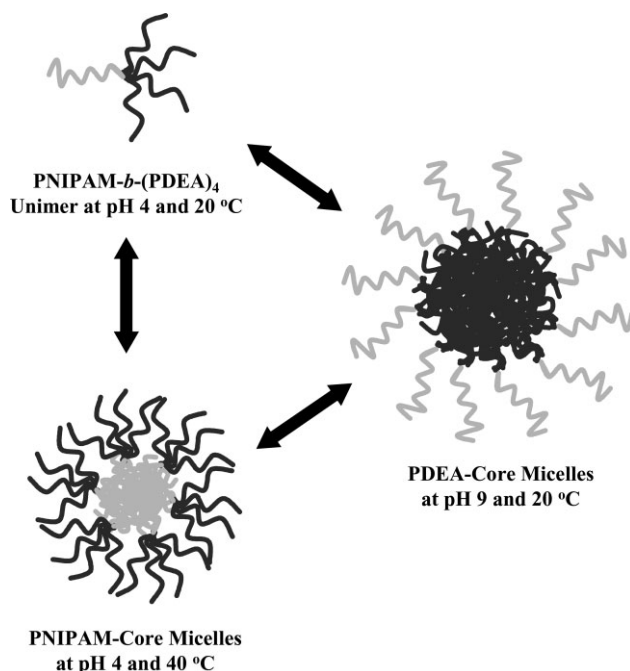


Figure 2. Schematic illustration of dually-responsive “schizophrenic” micellization behavior of AB₄ miktoarm star copolymer, PNIPAM-*b*-(PDEA)₄, in aqueous solution.

with double-exponential functions, yielding a fast (τ_1) and a slow (τ_2) relaxation processes. τ_1 for both copolymers decreased with increasing polymer concentrations. τ_2 was independent of polymer concentration for PNIPAM₆₅-*b*-(PDEA₆₃)₄, whereas it decreased with increasing polymer concentrations for PNIPAM₇₀-*b*-PDEA₂₆₀. This further indicated that pH-induced self-assembly of nonlinear and linear block copolymers follow distinctly different kinetic pathways.

A_nBA_n Miktoarm Star Copolymers

Amphiphilic A_nBA_n miktoarm star copolymers were typically synthesized via anionic polymerization, controlled free radical polymerizations, ROP, click reaction or a combination of them.^[79–83] A recently example was reported by Pan and coworkers.^[83] They synthesized amphiphilic H-shaped block copolymers of 3-trimethoxylsilylpropyl methacrylate and ethylene oxide with varying block compositions, (PTMSPMA)₂-*b*-PEO-*b*-(PTMSPMA)₂. It was found that the obtained H-shaped miktoarm star copolymers can form a range of nanostructured aggregates, such as large compound vesicles (LCVs), multilayer vesicles and unilamellar vesicles. Most importantly, these intriguing nanostructures can be further structurally fixed via the sol-gel reaction of PTMSPMA segments, forming stable organic/inorganic hybrid supramolecular assemblies.

Previously, we reported the synthesis and self-assembly of nonlinear DHBCs of A₂BA₂ and A₄BA₄ types, i.e., H-shaped (PDEA)₂-*b*-PPO-*b*-(PDEA)₂ and star-*b*-linear-*b*-star type (PDEA)₄-*b*-PPO-*b*-(PDEA)₄ block copolymers.^[84] At pH 8.5 and 5 °C, (PDEA)₂-*b*-PPO-*b*-(PDEA)₂ and (PDEA)₄-*b*-PPO-*b*-(PDEA)₄ form much larger PDEA-core micelles, compared to linear PPO-*b*-PDEA with comparable PPO and PDEA contents. The formed PDEA-core micelles are expected to adopt a “flower-like” structure in which the soluble PPO central block forms loops stabilizing the insoluble PDEA core. In marked contrast to linear PPO-*b*-PDEA, upon heating the aqueous solutions at pH 6.4, both types of nonlinear block copolymers form unimolecular micelles with the core consisting of a single collapsed PPO chain. It should be noted that the formation of unimolecular micelles from super-H-shaped (PI)₃-*b*-PS-*b*-(PI)₃ in selective solvent, *n*-decane, has been previously reported by Hadjichristidis and coworkers.^[85]

ABC Miktoarm Star Terpolymers

When three types of polymer sequences are arranged in a nonlinear fashion, the simplest form would be ABC miktoarm star terpolymers.^[42,48,86,87] Notable examples concerning their supramolecular self-assembly in aqueous solution have been reported by Lodge and coworkers.^[88–93] They observed that miktoarm star terpolymers consisting of PEO, perfluorinated polyether and hydrogenated polybutadiene arms can self-assemble into a variety of morphologies ranging from discrete multicompartment micelles, extended wormlike structures with segmented cores, polygonal bilayer sheets and laterally nanostructured vesicles, depending on the relative block lengths. These robust nanostructured morphologies are considered to be associated with the unique miktoarm star topology and intrinsic incompatibility between perfluorinated polyether and hydrogenated polybutadiene within hydrophobic micelle cores or vesicle bilayers. Just recently, Zhang et al.^[94] reported the synthesis of amphiphilic ABC miktoarm star terpolymers, PS(*b*-PNIPAM)-*b*-PCL, via a combination of ATRP, ROP and consecutive click reactions. In aqueous solution, the obtained amphiphilic miktoarm star terpolymers self-assemble into spherical micelles possessing mixed PS/PCL cores and thermo-responsive PNIPAM coronas.

We recently reported the first two examples of stimuli-responsive double hydrophilic ABC miktoarm star terpolymers, PEO(*b*-PMAA)-*b*-PDEA and PEO(*b*-PDEA)-*b*-PNIPAM, where PMAA stands for poly(methacrylic acid).^[95,96] Bearing pH-responsive PMAA and PDEA arms, well-defined PEO(*b*-PMAA)-*b*-PDEA miktoarm star terpolymers self-assemble into three types of micellar aggregates by simply adjusting solution pH at room temperature. Above pH 8, PDEA-core micelles stabilized

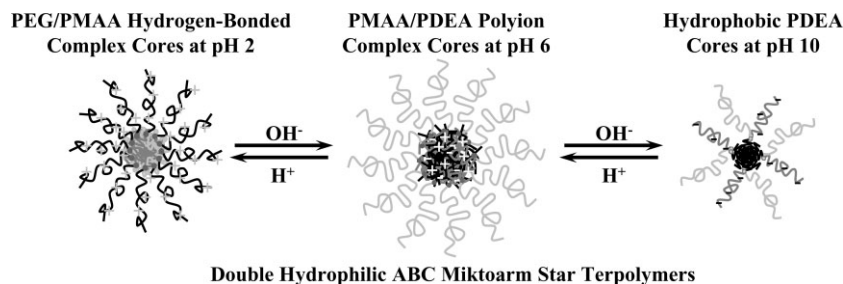


Figure 3. Schematic for pH-responsive formation of three types of micellar aggregates from PEO(-*b*-PMAA)-*b*-PDEA zwitterionic ABC miktoarm star terpolymers in aqueous solution.

by PEO/ionized PMAA hybrid coronas form due to insolubility of PDEA block. In a pH range of 5–7, micelles possessing polyion complex cores formed due to charge-compensation between partially ionized PMAA and partially protonated PDEA sequences. At pH < 4, hydrogen bonding interactions between fully protonated PMAA and PEO led to the formation of another type of micellar aggregates possessing hydrogen-bonded complexes cores stabilized by protonated PDEA coronas (Figure 3).

When one of the arms of ABC miktoarm star copolymers was replaced by functional moieties such as C₆₀, their supramolecular self-assembly can facily lead to its spatial ordering. Wang et al.^[97] synthesized well-defined amphiphilic block copolymer incorporated with a single C₆₀ moiety at the diblock junction point, PEO(-*b*-C₆₀)-*b*-PS. The obtained C₆₀-containing amphiphilic diblock copolymer self-assembles in aqueous solution into fullerene-containing hybrid vesicles. We thus successfully demonstrated that block copolymer self-assembly can be utilized to tune the spatial arrangement of C₆₀, which might further broaden the application scopes of fullerenes (Figure 4). By changing the relative block lengths of PEO and PS blocks, we expect that hybrid nanostructures with more complex morphologies embedded with orderly arranged C₆₀ could be obtained.

Dendritic–Linear Block Copolymers

Dendritic–linear and dendritic–linear–dendritic block copolymers combine advantageous properties of two types of macromolecular architectures (linear and dendritic), and the latter are also called dumbbell-shaped ABA block copolymers. The self-assembling behavior of amphiphilic dendritic–linear copolymers in aqueous solutions has been extensively investigated.^[98–100] Gitsov et al.^[101] reported that dendritic–linear–dendritic copolymers consisting of poly(benzyl ether) dendrimers and PEO building blocks can self-assemble into multimolecular aggregates in aqueous solution, which exhibit excellent loading capacity for hydrophobic small molecules. Adeli et al.^[102] reported the

synthesis and self-assembly of dendritic–linear–dendritic triblock copolymers consisting of dendritic triazine and PEO segments.

Amphiphilic dendritic–linear block copolymers consisting of stimuli-responsive hydrophilic segments have also been reported. Fréchet et al. synthesized dendritic–linear block copolymers comprising PEO and dendritic polylysine or polyester.^[103] At first, the dendritic moiety was rendered water-insoluble by grafting hydrophobic functionalities at

its periphery via highly acid-sensitive cyclic acetal linkages. These copolymers can form stable aggregates in aqueous solution at neutral pH but spontaneously disintegrate into unimers at mildly acidic condition due to the loss of hydrophobic groups upon acetal hydrolysis. Thus, this novel type of self-destructive aggregates could serve as smart nanocarriers for the controlled-release of hydrophobic drugs at targeted sites (Figure 5).

Ge et al.^[104] synthesized dendritic–linear diblock copolymers consisting of third generation poly(benzyl ether) dendrimer, [G-3], and PNIPAM via the RAFT technique, which can self-assemble in aqueous solution into polymeric micelles with a compact hydrophobic core of [G-3] stabilized by thermo-responsive PNIPAM coronas. By

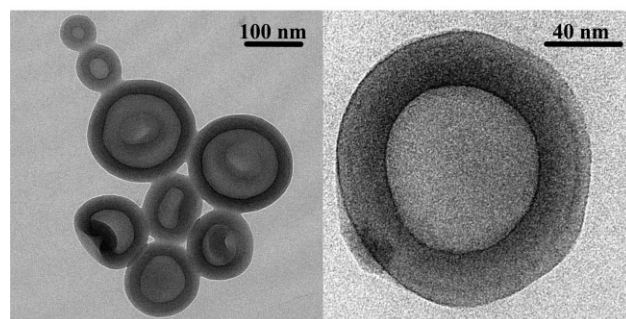
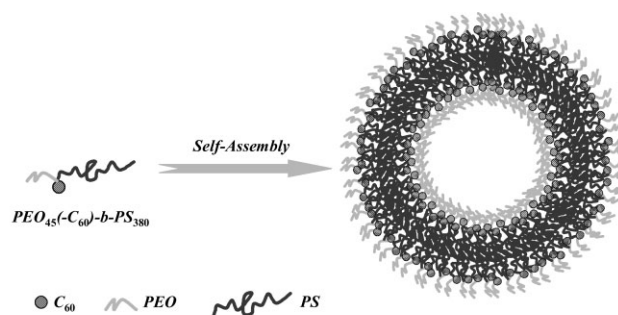


Figure 4. Schematic for the fabrication of fullerene-containing hybrid vesicles via the self-assembly of PEO(-*b*-C₆₀)-*b*-PS in aqueous solution and typical HRTEM images of fullerene-containing hybrid vesicles self-assembled from PEO₄₅(-*b*-C₆₀)-*b*-PS₃₈₀ in aqueous solution.

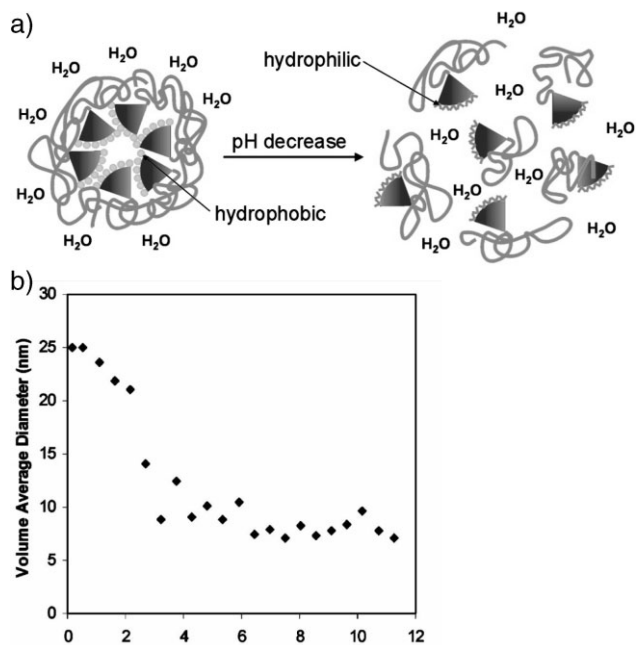


Figure 5. a) Schematic for drug release from pH-responsive micelles self-assembled from dendritic-linear block copolymers comprising PEO and either a polylysine or polyester dendrimer. b) Time-dependent size decrease of aggregates (pH 5.0 and 37 °C) formed from dendritic-linear block copolymers comprising PEO and polylysine dendrimer surface modified with acid-sensitive acetal moieties. Reproduced with permission from ref.^[103] Copyright 2004 the American Chemical Society.

employing a combination of LLS and excimer fluorescence measurements, they observed that soluble PNIPAM chains are sparsely anchored at the surface of porous core and the thermo-responsive collapse of PNIPAM coronas was a two-stage process. Furthermore, dumbbell-shaped tri-block copolymer, [G-3]-PNIPAM-[G-3] was also prepared employing [G-3]-based trithiocarbonate as the mediating agent.^[105] In aqueous solution, it self-assembles into spherical nanoparticles with the core consisting of hydrophobic [G-3] and coronas of the central PNIPAM blocks, which form loops surrounding the insoluble core.

Two notable examples have been reported for the self-assembly of double hydrophilic dendritic-linear block copolymers. Hammond et al.^[106] synthesized dendritic-linear-dendritic block copolymer composed of linear PPO and poly(amidoamine) dendrimer (PAMAM) with varying generations. They can form stable aggregates in aqueous media with relative low CMC and high loading efficiency, which can be further tuned by the PAMAM generation, pH, or ionic strengths. Park et al.^[107] reported that double hydrophilic dendritic-linear-dendritic copolymer, PAMAM-*b*-PEO-*b*-PAMAM, can efficiently form compact and nanoscale-sized water-soluble particles upon complexation with plasmid DNA and high transfection efficiency has been achieved.

Cyclic Block Copolymers

The unique “endless” topology endows cyclic polymers with distinctly different physical properties in solution and bulk as compared to their linear counterparts.^[108] However, literature reports concerning the supramolecular self-assembly of amphiphilic and double hydrophilic cyclic block copolymers are relatively rare, possibly due to synthetic difficulties encountered in their synthesis. In 1996, Deffieux et al.^[109] reported the synthesis of tadpole-shaped amphiphilic block copolymers comprising cyclic poly(hydroxyethyl vinyl ether) (PHEVE) and linear PS. Later, they prepared a series of narrow-disperse cyclic diblock copolymers consisting of PS and PEO blocks via intramolecular cyclization of linear α -diethyl acetal- ω -styrenyl PS-*b*-PEO precursors under high dilution conditions.^[110] However, their supramolecular self-assembly in aqueous solution has not been reported in both examples. Just recently, Pan et al.^[111] reported the synthesis of amphiphilic tadpole-shaped copolymers consisting of linear PNIPAM and cyclic PS blocks by coupling RAFT polymerization and click chemistry. Compared to linear PNIPAM-*b*-PS block copolymers, thin films of tadpole ones exhibit considerably higher water contact angles.

Xu et al.^[112,113] recently reported the synthesis of well-defined *cyclic*-PNIPAM via a combination of ATRP and click chemistry. Possessing no chain ends, *cyclic*-PNIPAM exhibits unique thermal phase transition behavior, when compared to linear PNIPAM with the same MW. Typically, the former exhibits a lower LCST, stronger concentration dependences of LCST and smaller enthalpic changes (ΔH) associated with the thermal phase transition.^[114,115] *Cyclic*-PNIPAM also possesses drastically different aggregation properties in aqueous solution. A comparative study of thermo-induced association of linear and cyclic PNIPAM in the slow and fast heating processes shows that the initial chain configuration (topology) exerts a huge effect on how these PNIPAM chains can aggregate together to form stable mesoglobules in dilute aqueous solutions. When the solution is heated above the LCST, linear PNIPAM chains simultaneously undergo intrachain contraction and interchain association/entanglement to form large and dense aggregates whose size increases with the solution temperature. In contrast, *cyclic*-PNIPAM chains tend to form smaller and stable mesoglobules with a relatively lower chain density, presumably due to the lack of interchain entanglement and penetration. The fast heating on a stopped-flow temperature-jump device shows that a sudden heating of *cyclic*-PNIPAM chains in a dilute solution leads to large, unstable, and loose aggregates that subsequently undergo fragmentation, resulting in smaller and stable mesoglobules made of individual collapsed single-chain globules.^[112]

In the context of double hydrophilic cyclic diblock copolymers, Ge et al.^[116] recently reported a novel strategy

for the high-efficiency preparation of cyclic diblock copolymers at relatively high concentrations via the combination of supramolecular self-assembly and “selective” click reactions, relying on the fine control of spatial accessibility between terminal reactive groups. It was found that thermoresponsive cyclic diblock copolymers typically self-assemble into aggregates at elevated temperatures, which possess higher CMC values, a smaller size and lower average aggregation numbers, when compared to those of their linear precursors.

Comb-Shaped Copolymer Brushes

Possessing a high density of side chains covalently attached to linear backbones, comb-shaped polymer brushes have been the subject of continuously increasing interest due to their unique extended cylindrical conformation in a good solvent, which is drastically different from the random coil conformation adopted by conventional polymers.^[117] The categorization, synthesis, solution properties and aggregation behavior of polymer brushes have been detailed in several recent review articles.^[46,118–120] Here we only summarize some recent developments in the supramolecular self-assembly of copolymer brushes comprising two different types of polymer grafts arranged in an alternating or “centipede” manner.

Alternating Copolymer Brushes

Alternating copolymer brushes typically consist of two types of chemically different homopolymer side chains alternatively distributed along the backbone. Previous literature reports in this aspect mainly focus on amphiphilic alternating copolymer brushes, bearing hydrophilic and hydrophobic side chains.^[121–124] Ishizu et al.^[125] reported the synthesis of amphiphilic alternating copolymer brushes via free-radical alternating copolymerization of vinylbenzyl-terminated PS and methacryloyl-terminated PEO in the presence of Lewis acid (SnCl_4). In aqueous solution, they self-assemble into large, rod-like aggregates. By employing a similar synthetic strategy, alternating copolymer brushes consisting of PPO and PEO segments were also prepared, which self-assemble into rod-like or irregular aggregates in aqueous solution, depending on the overall polymer concentration.^[126]

Just recently, we prepared well-defined amphiphilic copolymer brushes possessing alternating PMMA and PNIPAM

grafts, poly(PMMA-*alt*-PNIPAM), via a combination of ATRP and click chemistry.^[127] In aqueous solution, poly(PMMA-*alt*-PNIPAM) alternating copolymer brushes self-assemble into stable spherical aggregates consisting of hydrophobic PMMA cores and densely grafted thermo-responsive PNIPAM coronas. Compared to that of linear PNIPAM with similar a MW, PNIPAM chains densely packed in the micelle corona possess lower phase transition temperature and smaller ΔH .

Centipede-Shaped Copolymer Brushes

Centipede-shaped copolymer brushes represent a novel type of copolymers brushes, in which two side chains are connected at each grafting point along the backbone and the spacing between neighboring grafting points is constant.^[128,129] When the two side chains attached to the same grafting point are chemically different, they are called as asymmetric centipede-shaped copolymer brushes.^[130,131] Huang et al.^[132] recently synthesized well-defined centipede-shaped amphiphilic copolymer brushes bearing hydrophilic PEO and hydrophobic PS side chains via a consecutive ATRP technique. In aqueous solution, they self-assemble into stable spherical aggregates.

We recently reported the synthesis of coil-rod double hydrophilic diblock copolymer, PEO-*b*-[PGMA-*g*-(PDEA)(PMEO₂MA)], with dually-responsive asymmetric centipede-shaped copolymer brush as the rod segment via a combination of ATRP and click chemistry, where PGMA and PME₂MA are poly(glycidyl methacrylate) and 2-(2-methoxyethoxy)ethyl methacrylate, respectively.^[133] Atomic force microscopy (AFM) analysis revealed that

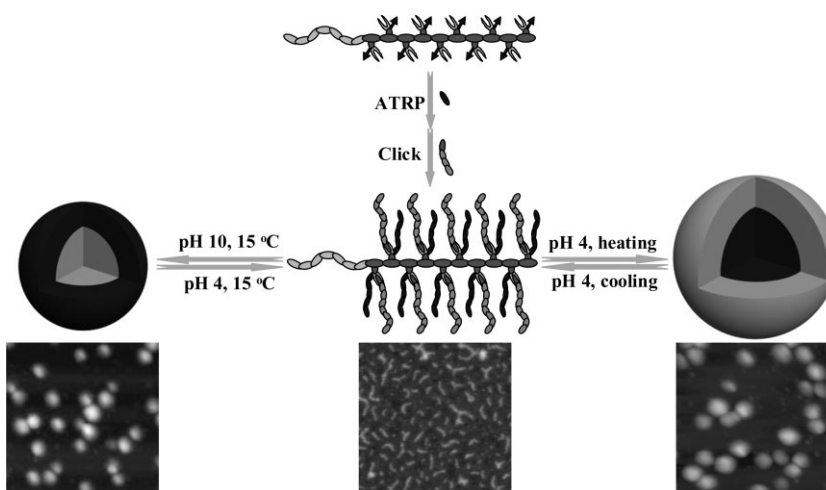


Figure 6. Schematic illustration of multi-responsive supramolecular self-assembly of coil-rod double hydrophilic diblock copolymer, PEO-*b*-[PGMA-*g*-(PDEA)(PMEO₂MA)], and typical AFM height images of self-assembled aggregates obtained at different conditions in aqueous solution.

PEO-*b*-[PGMA-*g*-(PDEA)(PMEO₂MA)] coil-rod diblock unimolecular chains adopt a worm-like conformation in aqueous solution at pH 4 and room temperature. Possessing pH-responsive PDEA and thermo-responsive PME₂MA grafts arranged in an asymmetric centipede manner within the rod segment, PEO-*b*-[PGMA-*g*-(PDEA)(PMEO₂MA)] self-assembles into two types spherical aggregates in aqueous solution at pH 10, 15 °C and pH 4, 40 °C, respectively (Figure 6).

Conclusion

In this feature article we summarize recent developments in the supramolecular self-assembly of amphiphilic and double hydrophilic block copolymers possessing nonlinear chain topologies, including miktoarm star polymers, dendritic-linear block copolymers, cyclic block copolymers, and comb-shaped copolymer brushes. It is noteworthy that this field is just at its very beginning. Most relevant examples have focused on the synthetic chemistry side, and less attention has been paid to their supramolecular self-assembly in selective solvents. We expect that further investigations will help elucidate the close relationship between their chain architectures and self-assembling properties.

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