Hyperbranched polymers: Advances from synthesis to applications

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Hyperbranched Polymers: Advances from Synthesis to Applications

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Hyperbranched polymers (HPs) are highly branched three-dimensional (3D) macromolecules. Their globular and dendritic architectures endow them unique structures and properties, such as abundant functional groups, intramolecular cavities, low viscosity, and high solubility. HPs can be facilely synthesized via one-pot polymerization of traditional small molecular monomers or emerging macromonomers. The great development in synthetic strategies, covering from click polymerization (i.e., copper-catalyzed azide-alkyne cycloaddition, metal-free azide-alkyne cycloaddition, strain-promoted azide-alkyne cycloaddition, thiol-ene/yne addition, Diels-Alder cycloaddition, Menschutkin reaction, aza-Michael addition, *etc*.) to recently reported multicomponent reaction, gives rise to diverse HPs with desirable functional/hetero-functional groups and topologies such as segmented or sequential ones. Benefiting from tailorable structures and correspondingly special properties, the achieved HPs have been widely applied in various fields, such as light-emitting materials, nanoscience and technology, supramolecular chemistry, biomaterials, hybrid materials and composites, coatings, adhesives, modifiers, and so on. In this review, we mainly focus on the progress in the structural control, synthesis, functionalization, and potential applications of both conventional and segmented HPs reported over the last decade.

1. Introduction

The world is branching. From non-living to living objects, branching occurs anywhere and anytime, such as the Crab Nebula, forked lightning, river basins, trees, nervures, nerves, veins, and proteoglycan ranging from light-years to kilometers, and to microscale and nanoscales (see Fig. 1). Hence, branching is a general and important phenomenon that could result in faster and more efficient transfer, dissipation, and distribution of energy and/or matter.[1]

As the fourth subcategory of polymer structure following linear, crosslinked, and chain-branched, dendritic polymers have greatly evolved from theory to practice.

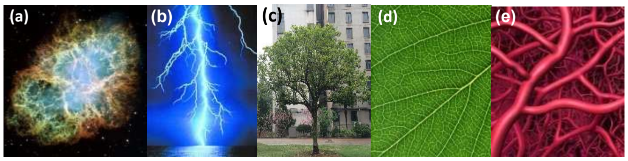
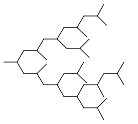
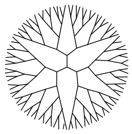


Fig. 1 Selected branching patterns observed in universe and nature: Crab Nebula (a), forked lightning (b), trees (c), nervures (d), vascular network (e). All images except c were obtained from the Internet.

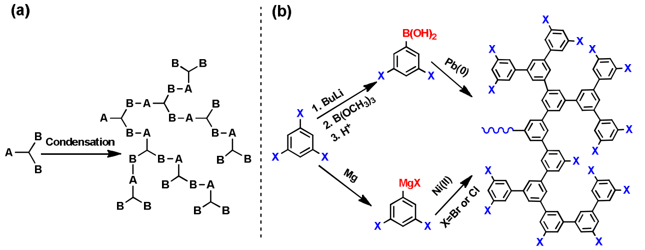
As one main subclass of dendritic polymers, HPs are a kind of randomly branched molecules with molecular size generally ranging from several to dozens of nanometers. Another main subclass of dendritic polymers is dendrimers with regularly branched and uniform structures. The differences among linear polymers, HPs, and dendrimers are listed in Table 1.[2] Generally, HPs possess irregular topology, functional groups at both linear and terminal units, low viscosity, and high solubility.

Table 1 Comparison of HP with linear polymer and dendrimer.

Polymer	Linear	Hyperbranched	Dendrimer
Structure			
Topology	1D, linear	3D, irregular	3D, regular
Synthesis	One-step, facile	One-step, relatively facile	Multi-step, laborious
Purification	Precipitation	Precipitation or classification	Chromatography
Scaling-up	Already, easy	Already, easy	Difficult
MW	Discrepant	Discrepant	Identical
PDI	>1.1	>1.1	1.0 (<1.05)
DB	0	0.4-0.6	1.0
Entanglement	Strong	Weak	Very weak or no
Viscosity	High	Low	Very low
Solubility	Low	High	High
Functional group	At two ends	At linear and terminal units	On periphery (terminal units)
Reactivity	Low	High	High
Strength	High	Low	Very low

By far, all the reported synthesized HPs could fall within two main categories, compact HPs (CHPs) and segmented HPs

(SHPs).[3,4] CHPs refer to the type of HPs with single or several repeating units between two branching points. Compact branching architecture and peripheral functional groups are their typical features. SHPs are analogues of CHPs, with long linear segments dispersed between every two branching points. Compared with CHPs, SHPs possess a sparsely branched framework and reactive groups may locate on the periphery and exist in the inner of SHPs.



Scheme 1 Theoretical model of Flory for synthesis of HPs (a)[6] and Kim-Webster's hyperbranched polyphenylene prepared by Suzuki polycondensation of AB_2-type monomer (b)[7].

In the early 20th century, Swedish chemist Jöns Jacob Berzelius first described the resin synthesized from tartaric acid (A_2B_2 type monomer) and glycerol (B_3 type monomer).[5] In 1952, by theoretical calculation, Flory predicted that highly branched polymers can be successfully synthesized by polycondensation of an AB_n ($n \geqslant 2$) monomer without the risk of gelation (Scheme 1a).[6] Until the late 1980s, Kim and Webster proposed the terminology of "hyperbranched polymers" as dendritic macromolecules with random branch-on-branch topology prepared by only one-step polymerization (Scheme 1b).[7] Prior to Kim's definition, Kricheldorf and co-workers even prepared branched copolymers by one-step copolymerization of AB- and AB_2-type monomers in 1982.[8] Afterwards, this area has been intensely explored, especially within the latest 25 years.

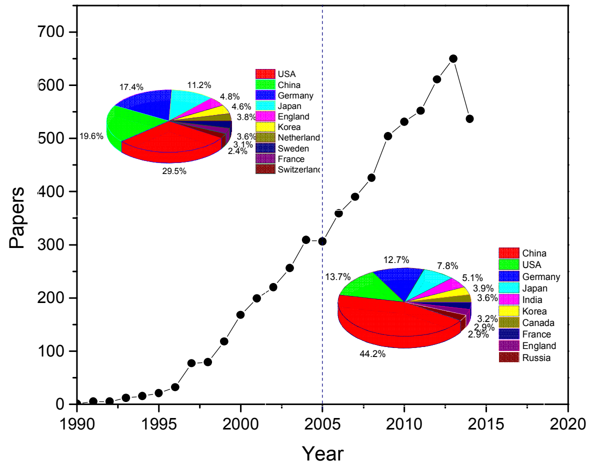


Fig. 2 Publication numbers during 1990 and 2014 with the topic of "hyperbranched polymers" searched by ISI Web of Science. Inset (left) shows the publication contributions of the top ten states form 1990 to 2005; and insert (right) shows those from 2005 to 2014.

As shown in Fig. 2, the number of published papers rises monotonously, witnessing the rapid development of HPs in synthesis, modification and potential application since 1990. The achievements can be summarized as the following major aspects: 1) synthesis: both polymer diversity and synthesis methodology are highly developed; 2) characterization: degree of branching (DB) can be determined accurately and controlled to some extent; 3) theory: polymerization kinetics has been theorized and used to calculate molecular parameters of HPs; 4) hyperbranched architecture: new highly branched structures are presented and prepared; 5) surface modification: multifunctional surfaces ranging from nanoforests to polymer brushes are easily accessible; 6) nanotechnology: to be used as new building elements, reactors, and templates of nanomaterials and nanohybrids; 7) supramolecular self-assembly: represents new building blocks, new assembly mechanisms, and new assembly objects; 8) other diverse applications: ranging from functional materials, biomaterials, and coatings to additives.[1] All the progress has been well documented in the recently reported review articles[9-43] and the monograph edited by Yan, Gao and Frey.[1]

In this review, we focus on structure control methods, synthetic strategies (especially click polymerizations and click post-functionalizations), and applications of both CHPs and SHPs developed in the last decade.

2. Structure of HPs

2.1 DB

Highly branching is the important character of HPs, which makes them unique from linear macromolecules and crosslinked networks. Generally, DB was defined as the ratio of molar fraction of branched and terminal units relative to that of total possible branching sites. The HP made from AB_2 type monomers may contain dendritic (D), terminal (T), linear (L) and initial (I) units (Fig. 3).

For the polycondensation of AB_2 type monomer, DB can be calculated approximately from the eq. 1:[44-47]

$$\mathrm{DB} = \frac{\mathrm{D}+\mathrm{T}}{\mathrm{D}+\mathrm{T}+\mathrm{L}} \qquad (1)$$

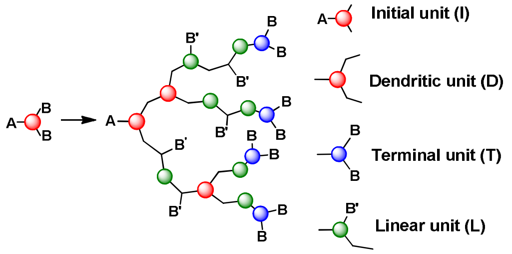


Fig. 3 Different units in HPs made from AB_2 type monomer.

As the HP with high degree of polymerization (DP), the number of T approximates that of D. So, eq. 1 is simplified as,

$$\mathrm{DB} = \frac{2\mathrm{D}}{2\mathrm{D}+\mathrm{L}} = \frac{1}{1+\mathrm{L}/2\mathrm{D}} \qquad (2)$$

Although the accurate numbers of structural units are unknown, DB can be indirectly derived from the ratio of L/D by NMR measurements.

With regard to self-condensing vinyl polymerization of AB_2 inimer-type monomers, DB of HP largely depends on the reactivity ratio (γ) of two step reactions, which can be calculated by eq. 3. [45,46]

$$\overline{\mathrm{DB}} = \frac{4[(\gamma-1)(1-e^{-2z})+e^{-\gamma z}-1](\gamma-2+2e^{-\gamma z}-\gamma e^{-2z})}{(\gamma-2)^2(1-\{1-\frac{2}{\gamma-2}[(\gamma-1)(1-e^{-2z})+e^{-\gamma z}-1]\}(2-e^{-2z}))} \qquad (3)$$

Where, $\gamma = k_{A\text{-}B'}/k_{A\text{-}B}$; $k_{A\text{-}B'}$ and $k_{A\text{-}B}$ are reaction rate constants of A to B' and B groups (B' refers to the residual functional group on the linear unit, see Fig. 3); z is a dummy variable.

Extremely, as $\gamma = 0$, a linear polymer (DB = 0) is achieved; if γ approaches infinity, DB will reach 1. As $\gamma = 1$ (viz. B and B' groups with the equal reactivity), the dependence of average value of DB on the conversion (x) of A group can be simply expressed by eq. 4:[45,47]

$$\overline{\mathrm{DB}}_{\gamma=1} = \frac{2x}{5-x} \qquad (4)$$

When polycondensation approaches to completion, that is, $x \approx 1$, DB can reach 0.5, the maximum value for the case of equal reactivity.

In experiments, DB could be altered or tuned to some extent,[40,48-52] via four major methods: (i) copolymerization of AB_2 and AB monomers with different feed ratios;[53] (ii) changing the polymerization conditions such as temperature, feed ratio of monomer to catalyst, and solvent,[54-57] and the pressure of monomer;[58,59] (iii) host-guest inclusion of AB_2 or multifunctional monomer;[60] and (iv) combination of the above ones.

To enhance DB, five methods were tried: (i) increasing the reactivity of B' group;[61] (ii) addition of core molecules;[62] (iii) polycondensation of dendrons;[63] (iv) post-modification of the formed HPs to convert linear units to dendritic ones;[64] and (v) using special catalyst.[65] Through these techniques, DB could be obviously higher than 0.5 or even approach 1 in some cases.[65–71] Attentively, HPs still contain many isomers with different M_ws even though DB is equal to 1,[65,66] which is different from dendrimers that have the same MWs.

Direct and indirect methods have been set up to measure the DB of HPs. The direct methods include NMR measurements and degradation of polymer units. In the NMR measurements, both 1D[44] and 2D[60,72] techniques have been employed. Sometimes model compounds are required in order to correctly assign the signals of linear, dendritic, and terminal units and accurately calculate the integral. For the heteroatom-containing HPs, ^{15}N, ^{19}F, ^{29}Si, and ^{31}P NMR spectroscopies can been applied to calculate DBs.[73-77]

Except the NMR spectroscopy, the degradable approach has been also directly used to detect the DB of HPs. Hawker[78] and Wooley[79] degraded HP into L, D and T subunits which could be accurately detected by chromatographic analysis.

Furthermore, the indirect viscometry approach can be used to evaluate the DB of HPs based on the Mark-Houwink equation ($[\eta] = KM_{vis}^{\alpha}$),[4] since the relationship between intrinsic viscosity ($[\eta]$) and molecular weight (M_{vis}) of HPs is different from that of linear polymers.

2.2 MW

MW and polydispersity index (PDI) are other two significant parameters for HPs. Based on statistical and kinetic methods for HPs made by polycondensation of AB_g monomers, the dependance of DP and PDI on conversion of monomers has been summarized in Table 2.[80,81] Obviously, PDI increases with the increasing of conversion. Nevertheless, in experiments, the PDI could be narrowed by the techniques of (i) slow addition of monomers into reaction system,[82-86] (ii) copolymerization with core molecules,[84-90] and (iii) classification by the dialysis or precipitation.[1] It needs to mention that the monomer/core ratio (γ) has an effect on PDI, since the tendency of self-polycondensation of monomers can not be completely suppressed. As $\gamma < 100$, PDI is lower than 1.3, while $\gamma > 100$, PDI becomes broader.[40,84,89]

Table 2 DP and PDI of polymers synthesized from AB_g type monomers.

Monomer type	g = 1	g ⩾ 2
P_n	$1/(1-x)$	$1/(1-x)$
P_w	$(1+x)/(1-x)$	$(1-x^2/g)/(1-x)^2$
PDI	$1+x$	$(1-x^2/g)/(1-x)$

Yokozawa and colleagues successfully synthesized diverse HPs with the low PDIs (~1.13) and controlled MWs.[91-96] They attributed it to the improved reactivity of terminal groups by the condensation and considered the process of propagation to be carried out following the mechanism of controlled chain-growth polymerization.

Similarly, due to the controllable chain propagation, living /controlled polymerizations (such as anionic, cationic, and radical one) of AB_2 or latent AB_2 type monomers have been already utilized to prepare HPs with low PDI and controlled MWs.[97,98]

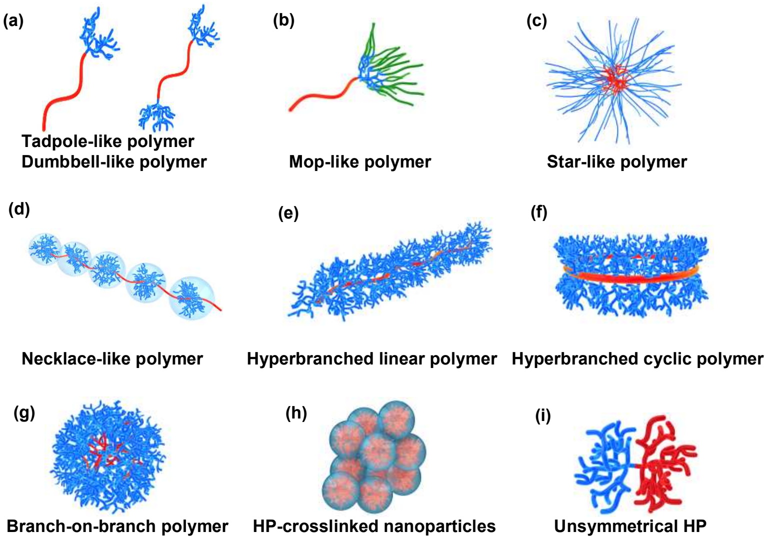


Fig. 4 HP-based complex polymeric structures.

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Typically, Brooks synthesized hyperbranched polyglycerol (HPG) with ultrahigh number-average molecular weight (up to 700,000 g mol^{-1}) and PDI of 1.1-1.4 by emulsion anionic polymerization of glycidol.[99]

2.3 Topology

Apart from the general compact/sparse branching structure of CHPs/SHPs, some complex topologies have been designed and prepared to meet various potential applications.[100,101] Generally, the complex topologies of HPs include two major types, which are linear-hyperbranched and hyperbranched-hyperbranched ones. Linear-hyperbranched polymer consists of both linear moiety and branched part, such as tadpole-like, dumbbell-like, mop-like, star-like, necklace-like, hyperbranched linear and hyperbranched cyclic ones (Fig. 4a-4f). The hyperbranched-hyperbranched polymer was composed of different branched spheres or hemispheres, including branch-on-branch polymer, HP-crosslinked particles, and unsymmetrical HP (Fig. 4g-4i).

3. Synthesis of CHPs

3.1 Synthesis methodologies

Various synthesis methods have been proposed to access CHPs. In terms of the number of monomer used in the polymerization, we classify them as four categories: single-monomer methodology (SMM), double-monomer methodology (DMM), couple-monomer methodology (CMM) and multi-component methodology (MCM) (Fig. 5).

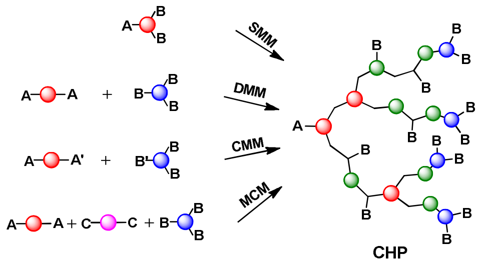
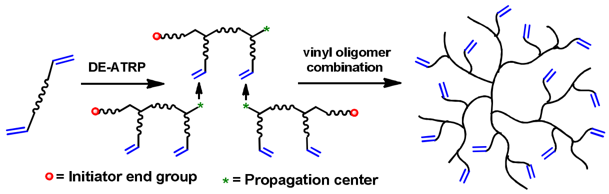


Fig. 5 Four kinds of synthesis methodologies for accessing CHPs.

For SMM, only one type of monomers (AB$_n$ or latent AB$_n$ type) is used in the polymerization. The SMM generally includes six types of polymerization techniques: (1) the classic step-growth AB$_n$ polycondensation, (2) self-condensing vinyl polymerization (SCVP), (3) self-condensing ring-opening polymerization (SCROP), (4) proton-transfer polymerization, (5) chain-walking polymerization (CWP), and (6) dialkyne polycyclotrimerization.

The step-growth AB$_n$ polycondensation is probably the most widely employed method to prepare HPs. Generally, the "n" equals 2. If both B groups can react with A group, it generates one branch unit. If only one B group of AB$_2$ monomer is reacted, it forms one linear segment. If none of B groups is reacted, this unit becomes a terminal one. Despite no risk of gelation in such a method, most of monomers need to be freshly synthesized.

SCVP was first invented by Fréchet in 1995,[102] using an inimer (AB*) to construct HPs. Here, A group represents a vinyl moiety and B* group refers to the initiating site. As the polymerization starts, the formed dimer (A-b-a*-B*, similar to the AB$_2$ monomer) contains one vinyl group and two initiating sites. Based on a broad variety of monomers, the SCVP approach greatly extended the amount and application of HPs.[15,103-108] Moreover, if combined with the controlled radical polymerizations, better controllability of the polymerization becomes accessible. Free radical polymerization of divinyl mononers was reported by Wang and co-workers.[109] This strategy of vinyl oligomer combination can overcome those shortcomings (such as the low DB and yield) involved in other synthetic approaches.[3,110] Through the kinetic theory to adjust chain growth conditions, the HP with DB of 0.66 and numerous vinyl functional groups was synthesized via deactivation-enhanced atom transfer radical polymerization (DE-ATRP) of the multi-vinyl monomers using ethyl 2-bromoisobutyrate (EBriB), copper (II) bromide/*N,N,N',N',N''*-pentamethyldiethylenetriamine (CuBr$_2$/PMDETA) as the initiator and catalyst, respectively (Scheme 2).



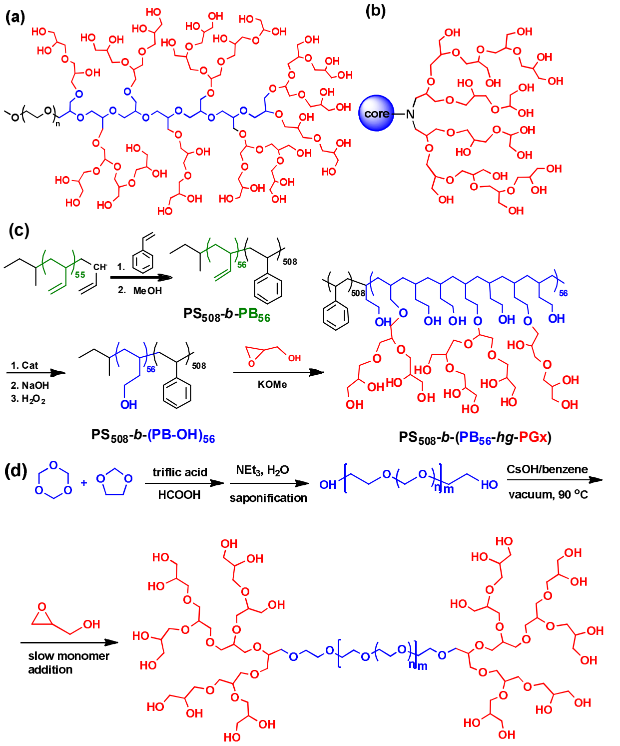
Scheme 2 HPs with abundant vinyl groups synthesized by the approach of vinyl oligomer combination.[109]

Via oxyanionic vinyl polymerization, commercially available hydroxyethyl methacrylate (HEMA) or poly(ethylene glycol) methacrylate (PEG-MA) was applied as inimers for the scalable synthesis of HPs.[111,112]

In 1999, Fréchet and Hedric simultaneously reported the SCROP for CHPs.[113,114] Frey reported the synthesis of HPG via anionic inimer mediated method,[115-120] affording diverse interesting topologies of HPGs (Scheme 3).[115-117] Typically, the hyperbranched-linear-hyperbranched triblock copolymer was composed of a linear poly(oxymethylene) block and double HPG blocks. Firstly, bishydroxy-functional poly(oxymethylene) was synthesized via cationic ring-opening copolymerization of trioxane and 1,3-dioxolane exploiting formic acid as a chain transfer agent. After hydrolysis of formate groups, linear poly(oxymethylene) was obtained and served as macroinitiator for subsequent anionic ring-opening polymerization of glycidol. The hyperbranched-linear-hyperbranched copolymers with PDIs of 1.31-2.01 and MWs of 6,100-22,900 g mol^{-1} exhibited an adjustable degree of crystallization and hydrophilicity.[120] Yan reported the cationic SCROP of 3-methyl-3-xetanemethanol to get HPs with different DBs and degree of crystallization.[118,119] Recently, several papers were published elaborating the synthesis and corresponding performance investigation of HPG.[121-129]

Besides, Fréchet developed the proton transfer polymerization for hyperbranched epoxy polymers by nucleophilic ring-opening reaction of an H-AB_2 monomer.[130] Zhu and Yan synthesized thermo-responsive HPGs via proton transfer polymerization of vinyl and hetero-ring groups of glycidyl methacrylate, which displayed a wide range of critical solution temperatures from 0 to 100 °C.[131,132]

Exclusively for hyperbranched polyethylenes or polyolefins, the CWP is a great development in the field of transition-metal catalyzed reaction. By finely tuning catalyst and ethylene pressure, Guan *et al.* discovered the topology of the product could change from linear to highly branching structure.[133,134]



Scheme 3 Typical topologies of HPGs: linear-HPG block copolymer (a)[115], core-HPG shell type block-copolymer (b)[116], linear-HPG block-copolymer through hypergrafting of one block (c)[117], and HPG-linear-HPG triblock copolymer.[120]

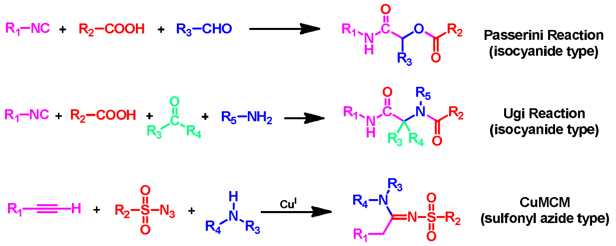
The polycyclotrimerization of dialkynes was developed by Tang's group.[135] Enlightened by the transition metal catalyzed alkyne cyclotrimerization, Tang and co-workers successfully synthesized soluble HPs under mild condition. They offered a new synthetic route for hyperbranched conjugated polymers.

For DMM, polycondensation of A_2 and B_3 type commercial monomers is the most utilized approach to achieve HPs.[136,137] Commonly, it needs to terminate the polymerization or add end-capping molecules prior to the critical point of gelation.

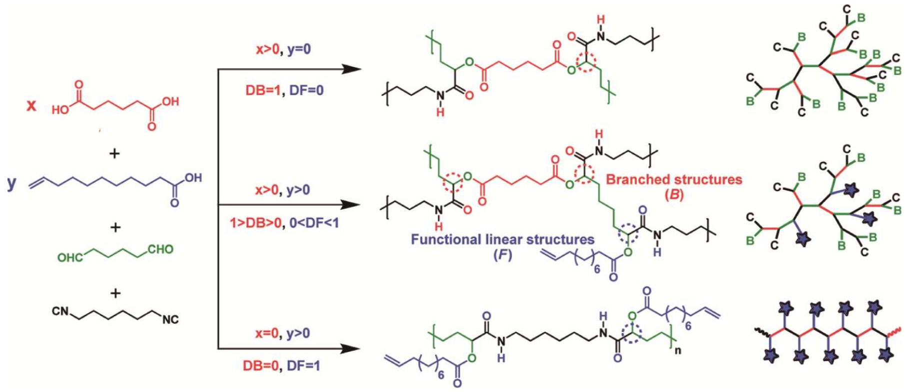
CMM approach is invented by Gao and Yan.[3] Based on the non-equal reactivity design of functional groups, it combinates the advantages of SMM and DMM. Specially, it can largely avoid gelation by direct polymerization of commercial monomers. For example, to an AA' + B'B_2 monomer pair (Fig. 5), in which group A' is more reactive than A or B' is more reactive than B, the faster coupling between A' and B' groups predominantly gives rise to an AB_2-like intermediate (A-a'b'-B_2) *in situ* at the early stage of reaction, making the smooth propagation in the manner of SMM subsequently.

The MCM employs three or more different monomers to prepare HPs in one-pot.[138-145] The multicomponent reaction (MCR) follows a step-growth reactive mechanism, giving the resulted HPs with the sequence-controlled architecture. For a three-component system (Fig. 5), the reaction of group A and C first generates highly reactive group D which subsequently reacts with group B, affording the target HPs. Notably, group A cannot directly react with group B, group B cannot directly react with group C, and only the intermediate group D can trigger the further polymerization.

The isocyanide-based (Passerini and Ugi reactions) and sulfoyl azide-based chemistries have been developed to synthesize HPs (Scheme 4).[139] The first three-component reaction of amine, aldehydes and hydrogen cyanide was used



Scheme 4 Isocyanide- and sulfonyl azide-type MCRs.[139]



Scheme 5 Synthesis strategy of HPs with tunable DB and DP values by Passerini MCM. Here, the star mark represents functional linear structure (F). (Reproduced from ref. 138, with permission from Royal Society of Chemistry.)

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to synthesize amino acids.[140] After that, multicomponent reaction has been successfully used for the preparation of monomers,[141] dendrimers,[142] segmented HPs,[139,140] and linear polymers[143] as well as the post-modifications.[144,145]

Just recently, Li's group reported MCM for HP synthesis.[138] As shown in Scheme 5, hexanedioic acid, hexane-1,6-dial, 1,6-diisocyanohexane and 10-undecenoic acid were copolymerized via Passerini reaction in one-pot. Through adjusting the feed ratio of starting materials, gelation was effectively avoided. Besides, the resulted topologies could be facilely tuned from the sequence controlled linear structure to segmented hyperbranched ones.

3.2 Synthesis by click polymerization

To meet increasing demands of sustainable and green polymer chemistry, chemists have been seeking to develop efficient chemical conjugation techniques featured with simplicity, reaction robustness and high atom economy. In this process, a number of classical or new chemistries come in front of people's eyes and their usages gradually become mature. The involved chemistries include amidation,[146] phosphation,[147] etherification,[148] esterification,[149] transetherification,[150] transesterification,[151] Knoevenagel reaction,[152] Suzuki/Heck/Friedel-Crafts/Sonogashira coupling,[153-156] hydrosilylation addition,[157] nucleophilic substitution,[158] nucleophilic ring opening,[159] electrophilic substitution,[160] electrophilic addition,[161] blocked isocyanate ring opening,[162] catalytic diene metathesis,[163] and supramolecular coupling,[164] *etc.*

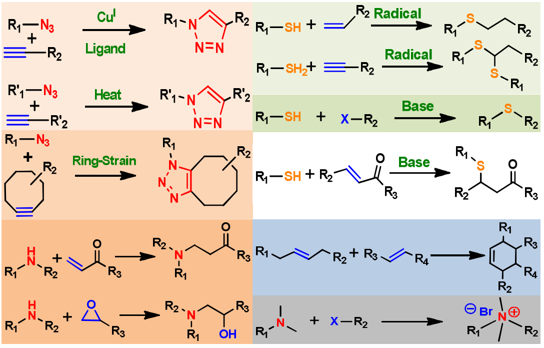


Fig. 6 Various kinds of click reactions for synthesis of HPs.

In this odyssey of exploring efficient chemistries, the proposition of the so-called "click chemistry" by Sharpless clearly marks a tuning point,[165] which offers a new philosophy of material design and inspires numerous efforts to look into the library of available reactions for developing more "click" or "click-like" chemistries.[166] Up to now, click chemistries have made a great contribution to the synthesis of HPs. Generally, it could be classified as three major types, which are cycloaddition, nucleophilic/electrophilic and radical-initiated click chemistries (Fig. 6). Cycloaddition click chemistries include copper-catalyzed alkyne-azide cycloaddition (CuAAC),[167] metal-free alkyne-azide cycloaddition (MFAAC),[168] strain-promoted cycloaddition (SPC)[169] and Diels-Alder reaction.[170] Nucleophilic click chemistries include thiol-click chemistry (thiol-epoxy reaction, thiol-isocyanate reaction, thiol-halogen reaction, and thiol-Michael addition)[171,172] and amino-click chemistry (amino-epoxy ring-opening reaction[173] and aza-Michael addition[174]). The recently reported Menschutkin quaternization can be belonged to the electrophilic click chemistry,[175] and thiol-ene/thiol-yne addition could be radical-initiated click chemistries.

Click polymerization, coined by Qin and Tang, brings influential revolution in both polymer synthesis and polymer post-modifications.[176] Employed monomers for HPs through click polymeriztions have been summarized in Tables 3-5.

3.2.1 CuAAC polymerization

CuAAC based AB_2 approach has been adopted to synthesize high-yield soluble azo-containing HPs, using two types of azo-chromophore AB_2 monomers (**M1** and **M2** in Table 3).[177, 178] To avoid possible cross-linking of the polymer caused by the peripheral azido groups, similar mono-alkynyl structures were introduced to end-cap the unreacted azido groups.[178] A new AB_2 monomer (**M3**) with fluoroaromatic groups was synthesized through the azo coupling method.[179] HPs were prepared using nonfluoro monomer **M2** and fluoro monomer **M3** via CuAAC chemistry, respectively. The as-synthesized polymers were either end-capped with non-fluoro mono-alkynyl azo chromophore or pentafluoroaromatic mono-alkynyl azo chromophore via secondary CuAAC. The fluoro-monomer decreased the chromophore loading density, which was popular for non-linear optical (NLO) properties.

Coexisting in AB_x type monomer, alkynyl and azide groups are reactive and can be consumed spontaneously during their preparation and storage. The A_x+B_y approach can solve this issue.[180-184] Slow addition of **M4** into the diluted solution of **M5** during A_2+B_3 CuAAC polymerization afforded soluble azobenzene-containing HPs with M_w of 15,000 g mol^{-1}, DB of 0.57 and yield of 65.5%.[180] Compared with linear analogues, they exhibited higher second-harmonic coefficient.[181] Using **M6** and **M7**, Qin and Tang prepared highly soluble and processable HPs with DB of ~0.90, which can be used as aggregation-induced emission (AIE) materials.[182-184] The conjugated HP with M_w of 39,000 g mol^{-1} was synthesized via CuAAC click polymerization of equally molar **M8** and **M9**. Due to the rigid hyperbranched structure, the HP exhibited a typical aggregation-enhanced emission (AEE) effect.

It is worth noting that CuAAC polymerization of electron-rich alkyne (such as **M7**) and azide was very slow (up to 7-10 days), implying CuAAC was alkyne-sensitive. Compared to copper catalyst [Cu(PPh$_3$)$_3$Br], the ruthenium catalyst (Cp*Ru(PPh$_3$)$_2$Cl or [Cp*RuCl$_2$]$_n$) exhibited better substrate tolerance and higher catalytic activity and yield (> 83%).[182] Moreover, employing ruthenium complex as catalyst, products were regioselective, affording solely 1,5-regioregular HPs.

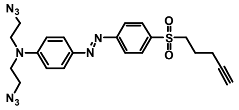
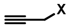
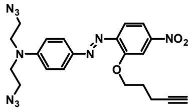
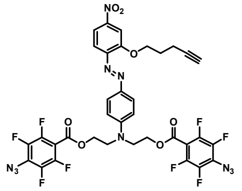
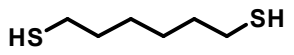
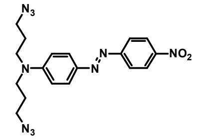
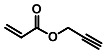
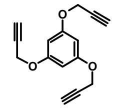
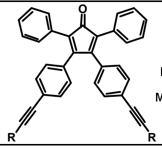
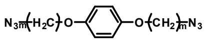
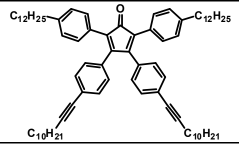
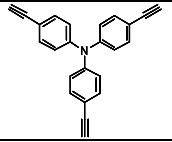
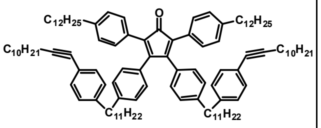
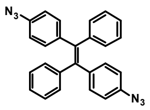
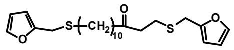
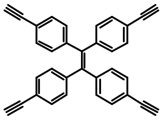
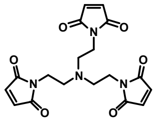
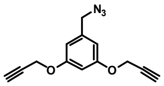
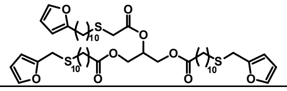
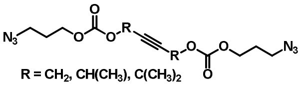
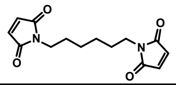
3.2.2 MFAAC polymerization

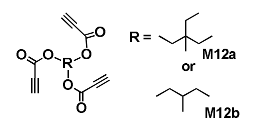
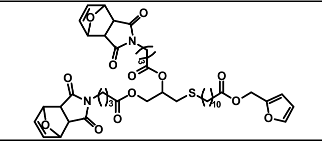
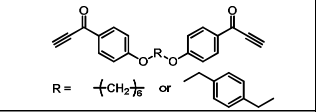
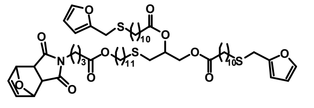
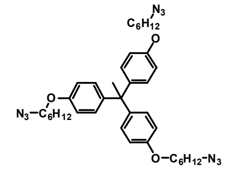
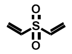
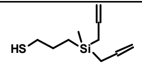
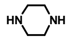
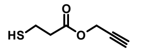
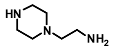
CuAAC exhibited high reactive efficiency, having been widely applied to synthesize polymers. However, involved metal ions are

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Table 3 Monomers used for click polymerization for CHPs.

	Structure	Type	Ref.		Structure	Type	Ref.
M1		AB_2 CuAAC	[177]	**M17**	 X = Br or Cl M17a M17b	CB_2 Thiol-halogen /Thiol-yne	[191]
M2		AB_2 CuAAC	[178]	**M18**	HS–R–SH R= $(CH_2)_3O(CH_2)_2O(CH_2)_3$; $(CH_2)_8$ M18a M18b	A_2 Thiol-halogen/Thiol-yne	[191]
M3		AB_2 CuAAC	[179]	**M19**		A_2 Thiol-ene/ Thiol-yne	[192]
M4		A_2 CuAAC	[180]	**M20**		CB_2 Thiol-ene/ Thiol-yne	[192]
M5		B_3 CuAAC	[180]	**M21**	 R = H, CH_3, C_6H_5 M21a, M21b, M21c	AB_2 Diels-Alder	[196]
M6		A_2 CuAAC	[182]	**M22**		AB_2 Diels-Alder	[197]
M7		B_3 CuAAC	[182]	**M23**		AB_2 Diels-Alder	[197]
M8		A_2 CuAAC	[183]	**M24**		A_2 Diels-Alder	[199]
M9		B_4 CuAAC	[183]	**M25**		B_3 Diels-Alder	[199]
M10		AB_2 CuAAC	[176]	**M26**		A_3 Diels-Alder	[199]
M11	 R = CH_2, $CH(CH_3)$, $C(CH_3)_2$ M11a, M11b, M11c	AB_2 TAAC	[185]	**M27**		B_2 Diels-Alder	[199]

M12		B_3 CuAAC	[186]	**M28**		Protected AB_2 Diels-Alder	[199]
M13		A_2 CuAAC	[187]	**M29**		Protected A_2B Diels-Alder	[199]
M14		B_3 CuAAC	[187]	**M30**		A_2 Aza-Michael	[200]
M15		AB_2 Thiol-ene	[189]	**M31**		B_2 Aza-Michael	[200]
M16		AB_2 Thiol-yne	[190]	**M32**		CB_2 Aza-Michael	[201]

very difficult to remove thoroughly, which limits the properties of photoelectric materials. Qin and Tang developed MFAAC strategy for conjugated HPs. Connected alkynyl or azide groups with electron withdrawing groups, such as carboxyl, ether bond, *etc.*, it can improve their reactivity largely, making MFAAC polymerization possible. If introducing sulphone groups with the stronger electron withdrawing capability into reactant, it will become easier.

In a preliminary study, the 3,5-bis(propargyloxy)benzyl azide (**M10**) was investigated for the polymerization behavior under Cu-catalyzed or metal-free condition[176]. Because of the high reactivity, **M10** needs to be stored below -20 °C. The CuAAC polymerization gives polymers with triazole ring of pure 1,4-isomer, while the MFAAC one affords products containing both 1,4-isomer and 1,5-isomer.

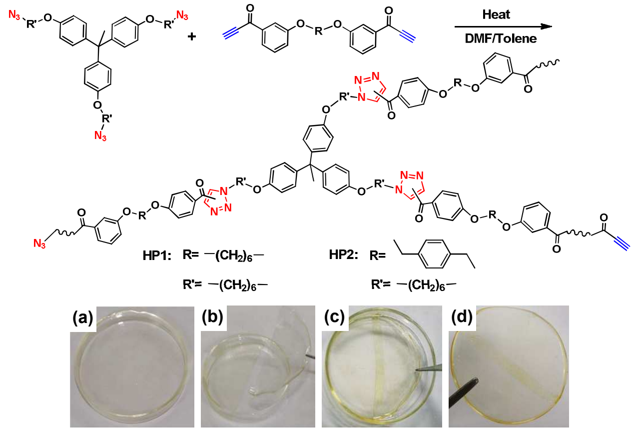


Fig. 7 Synthesis route of hyperbranched poly(aroyltriazole). The as-prepared film from hyperbranched poly(aroyltriazole) in petri-dish (a); the half-cut film (b); the self-healed film with overlapping width of 5 mm after heating (c); and the self-healed and stripped film (d). (Reproduced from ref. 187, with permission from Nature Publishing Group)

To avoid metal ions involved in products, researchers also explored the MFAAC polymerization between azides and 1,2-disubstituted triple bonds. Therefore, a series of AB_2 monomers (**M11a**, **M11b** and **M11c**) with two azido groups and one 1,2-disubstituted triple bond were synthesized to probe the polymerizability. After optimization, polymeriztion of **M11a** in bulk at 45 °C for several days and **M11b** in bulk at 60 °C for several hours yielded soluble products. This result was in accordance with the later report from Tang's group, which demonstrated that the effect of electron-withdrawing group on MFAAC.[176,185]

Recently, it was demonstrated that electron-withdrawing groups would be favorable for the regioselective [1+3] dipolar cycloaddition. **M12a** and **M12b** were used to carry out thermal alkyne-azide cycloaddition (TAAC) with **M8** in DMF at 60 °C. Strong electron-withdrawing ester groups in the used alkyne can activate and proceed A_2+B_3 click polymerization even if without metal ionic catalyst.[186] Bis(aroylacetylene)s (**M13a** and **M13b**) and triazide (**M14**) were designed and prepared for hyperbranched poly(aroyltriazole)s. Containing a large number of peripheral azido and alkynyl groups, the prepared film, when cut, could self-repair through TAAC at elevated temperature (Fig. 7).[187]

Nitrogen-rich HPs were prepared by polycyclotrimerization of dinitriles in 1,2-dichlorobenzene at room temperature, utilizing trifluoromethanesulfonic acid (CF_3SO_3H) as catalyst. Both Lewis and protonic acids are common catalysts for the cyclotrimerization of aromatic nitriles. Since the catalytic activity closely correlates with their strength, CF_3SO_3H with strong enough strength can accelerate cyclotrimerization effectively, affording heteroatom-containing hyperbranched polytriazine with high DB (about 0.63) and in high yield (~74.7%).[188]

3.2.3 Thiol-ene polymerization

In general, silicon-containing HPs were prepared through hydrosilylation using platinum catalyst. The rigorous reacting condition limited their applications. As an alternative approach, the photo-radical thiol-ene click polymerization were reported.[189] Via the thiol-ene click polymerization of **M15**, highly soluble silyl HPs were obtained, with numeraverage molecular weight (M_n) 3200 g mol^{-1} and PDI 1.78. The resulted polymer possesses large amount of allyl groups around the periphery, allowing the further functionalizations.

3.2.4 Thiol-yne polymerization

Thiol-yne polymerization is one of the newest synthetic techniques for HPs. AB_2 type thiol-yne monomer **M16** was reported by Perrier and co-workers.[190] Initiated by UV irradiation, thiol-yne polymerization was quickly carried out with the monomer conversion of 70% and 90% within 10 and 90 min. The resulted hyperbranched polythioether had a DB of 1.0.

Three major troubles are tangled in achieving the α-thiol-ω-alkynyl AB_2 type monomer for CHPs: 1) rarely commercial supply; 2) difficult synthesis; and 3) low yield.

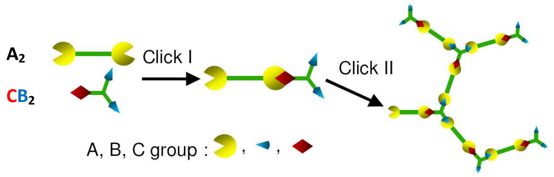
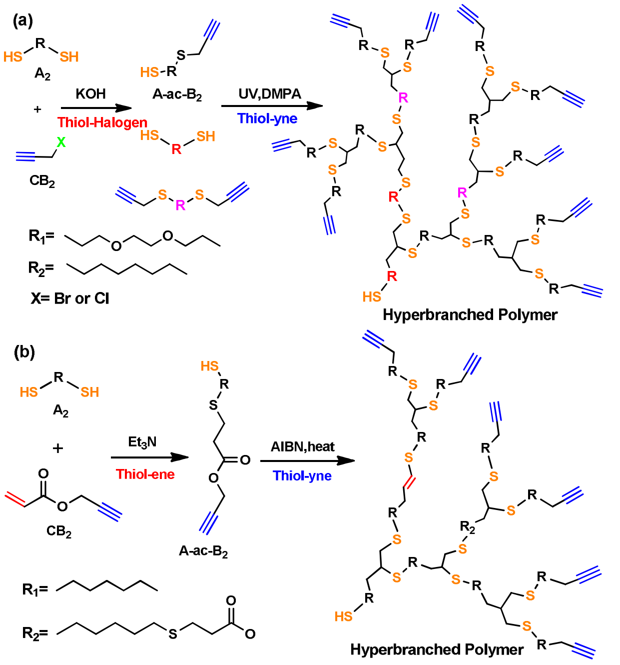


Fig. 8 All click reactions of CMM for synthesis of HPs.

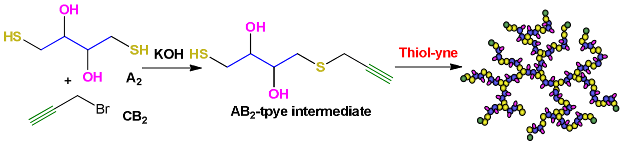
Gao *et al.* developed the synthesis of AB_2 type monomers via thiol-halogen reaction using commercially available reactants in one-pot manner. In ice bath, the solution of **M17** was slowly added into the mixture of **M18** and KOH to form the AB_2 type monomer (Scheme 6a). After the consecutive two-step thiol-yne addition reaction triggered by photointiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), hyperbranched polythioethers were achieved with M_w of as high as 230,000 g mol^{-1} and DB of 0.68~0.82.[191]



Scheme 6 CMM click polymerization based on sequential thiol-halogen/thiol-yne click polymerization (a)[191] and thiol-ene/thiol-yne click polymerization (b)[192].

As mentioned above, the preparation and storage of AB_2 are difficult for thiol-yne click polymerization. Gao and co-workers designed a CMM approach to split the AB_2 monomer into two parts which can selectively combine into an AB_2 type dimer. **M19** (A_2 monomer) and **M20** (CB_2 monomer) were employed to carry out thiol-ene click chemistry for AB_2 type dimer as shown in Scheme 6b and Fig. 8.[192] Then, AIBN was added to initiate sequential thiol-yne click polymerization. The M_w of the products ranged from 3,400 to 105, 000 g mol^{-1} with the DB of 0.76-0.91. The high DB was attributed to the greater ratio (about 3) of the sencond addition of thiol to vinyl sulfide (r_2) and the first one of thiol to alkyne (r_1).[193]

Similarly, employing the hydroxyl group-containing α-thiol-ω-alkyne AB_2 type monomer, the sequential hetero-functional HP with M_w of 4,800 g mol^{-1} and PDI of 1.27 was facilely achieved via the step-growth polymerization initiated by free radical (Scheme 7).[172]



Scheme 7 Synthesis of sequential hetero-functional HPs via the step growth thiol-yne polymerization.[172]

3.2.5 Diels-Alder cycloaddition

Initiated from the enlightening work of Stille *et al.*,[194] [2+4] Diels-Alder (DA) cycloaddition for HPs gradually become popular.[195] Three types of tetraphenyl AB_2 monomers (**M21a-M21c**) containing two dienophile function and one diene function were synthesized.[196] Repetitive intermolecular DA reactions of **M21a-M21c** afforded poly(ethynyl)-, poly(methylethyl)- and poly(phenylethynyl)-substituted hyperbranched polyphenylene. Their M_ns ranged from 2500 to 25100 g mol^{-1} with PDI of 1.66-6.85.

Utilizing the property of high packing density and processability, **M22** and **M23** were carried out polymerization within the channel of porous alumina membranes.[197] DB of hyperbranched polyphenylene could be regulated using an AB_2/AB monomer pair.[198]

Reactions between the derivatives of furan and maleimide follow the mechainism of Diels-Alder cycloaddtiotion. Due to the facility of synthesis of furan or maleimide derivative, diverse HPs can be prepared via furan/maleimide Diels-Alder click polymerization, including A_2+B_3 (**M24**+**M25**) and A_3+B_2 (**M26**+**M27**). Additionally, AB_2 or A_2B monomer was synthesized from retro-DA deprotection of **M28** or **M29**. Typically, the M_w of obtained HPs ranged from 35,000 to 67,000 g mol^{-1} with PDI of 2.0~3.2.[199]

3.2.6 Aza-Michael addition

Aza-Michael addition has been widely used to synthesize HPs prior to the concept of "click chemistry" being presented. Because of its high reactivity, atom economy, and high selectivity, recently, aza-Michael addition has been adopted as a kind of click reaction and employed to prepare novel polymers. Generally, electron-withdrawing groups, such as carboxyl and sulfone groups, jointed to carbon-carbon double bond (C=C) can greatly improve the reactivity of aza-Michael addition reaction between amine and C=C.

Aza-Michael addition is a typical CMM reaction.[3] **M30** (A_2 type monomer), **M31** (B_2 type monomer) and **M32** (CB_2 type monomer) were used to carry out aza-Michael addition.[200,201] The secondary amino hydrogen is more reactive than primary amino hydrogen. Therefore, during the early state of the polymerization, an A-ac-B_2 type intermediate was formed, which ensured the polymerization process without gelation.

Pan *et al*. reported topology of polymer was controlled by reaction temperature during aza-Michael addition of disulfide-containing diacrylate and *N*-methyl ethylenediamine (MEDA).[202] If reaction temperature is below 40 °C, the formed secondary amine is non-reaction, owing to too high steric hindrance. In this case, aza-Michael addition follows A_2+B_2 mechanism and results linear polymer. Elevating the temperature (beyond 48 °C), the formed secondary amine is activated and the addition carries out based on A_2+B_3 mechanism. Correspondingly, the highly branching structure is obtained.

Additionally, thiol-Michael addition of tri(2-mercaptoethyl) amine (TMEA) and ethylene glycol diacrylate (EGDA) was used to synthesize hyperbranched poly(amine-ester)s (HPET) at 50 °C.[203] Tertiary aliphatic amine in branching units greatly restrained the fluorescence quenching.

4. Synthesis of SHPs

4.1 Synthetic methodologies

SHPs are the long chain analogues of CHPs. The farther distence between two branching units endows SHP with the sparser structure. By far, two major synthetic routes toward SHPs are developed: macromonomer methodology via either polymerization of AB_2 type macromonomer[204-206] or copolymerization of A_2 + B_3 type (macro)monomers and small-monomer methodology.

Perrier and co-workers employed RAFT polymerization to prepare macromonomers, such as poly(divinyl benzene).[207] Two direct synthetic strategies including "core outward" and "periphery inward" have been designed to build SHPs via chain step-growth/branching reactions.[208]

The biggest issue of macromonomer methodology for SHPs is the isolation of residual macromonomers from products. Adopting highly efficient reaction, such as the robust click polymerization, can easily reach 100% conversion of monomers and facilely solve this problem.

4.2 Synthesis by click polymerization

4.2.1 CuAAC polymerization

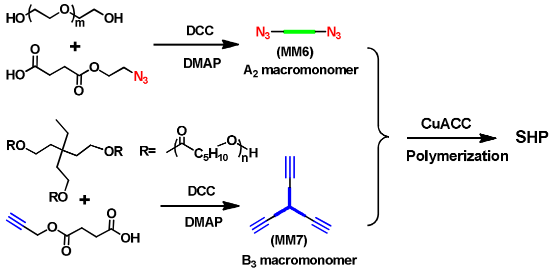
The Y-type AB_2 macromonomers (**MM1**, in Table 4) synthesized by ATRP of styrene possessed M_ns of 1,000, 3,300 and 7,300 g mol^{-1}. They were further used to carry out CuAAC polymerization, affording SHPs with M_ws of 82,000, 210,000 and 340,000 g mol^{-1} and corresponding PDIs of around 2. Interestingly, the macromonomer with lower M_w generated the SHP with larger M_w.[209] Two reactive alkynyls are so close to each other within Y-type AB_2 macromonomes. Once the first reaction is carried out, it will generate great steric hindrance for the subsequent click reaction. Hence, linear-units inevitably are involved in resulted SHPs.

Compared to Y-type AB_2 macromonomer, the seesaw-type one have a reactive group (A) in the middle of the long chain and two identical functional groups (B_2) at the both ends of two subchains. The specific structure of seesaw-type AB_2 macromonomers affords linear-unit-free (or defect-free) SHPs, making this synthetic strategy become more popular. ATRP of styrene and subsequent azidation of the bromo moieties generated **MM2**s (M_ws of 4,400, 10,000 and 18,000 g mol^{-1}) using the 1,3-dibromomethyl-5-propargyloxy-benzene (DBMPB) as difunctional initiator.[210] By CuAAC of **MM2**, SHPs were synthesized with M_ws of 900,000~1,400,000 g mol^{-1} (determined by GPC-MALLS). The results indicated that 10~20% macromonomers underwent intrachain reaction and longer sub-chain or higher **MM2** concentration effectively reduced cyclization. Intrachain clicking reactions (cyclizations) were evitable during the polymerization of seesaw-type AB_2 macromonomers, especially as the average degree of the self-polycondensation was high. Therefore, the achieved DB of SHPs synthesized by them shall be larger than that of SHPs made from Y-type AB_2 macromonomers.

Another polystyrene seesaw-type macromonomer **MM3** was synthesized by the similar strategy. The initial concentration of **MM3** has more obvious influence than its M_w on the rate of the polycondensation. The structure of the resulted SHPs was open and loose, controlled by the reaction-limited cluster-cluster aggregation mechanism.[211]

Macro-block-monomer (**MM4**) was synthesized via sequential ATRP of styrene and *tert*-butyl acrylate and subsequent azidation. CuAAC polymerization of **MM4** afforded diblock SHPs, hyper-(P*t*BA-PS-P*t*BA)s. As the *tert*-butyl group was hydrolyzed into acrylic acid, the amphiphilic hyper-(PAA-PS-PAA) was obtained. Dispersed in poor solvent for PS, the amphiphilic SHP tended to undergo intrachain folding of PS. When the concentration of SHP was > 50g L^{-1}, physical gel was formed.[212]

By the CuAAC polymerization between A_2 macromonomer (**MM5**) and B_3 monomer (**M34**), SHPs were synthesized with M_ws of 9,000-12,000 g mol^{-1}. The resultant SHPs showed a liquid crystalline characteristic of nematic phase and fast photo-response trans-cis isomerization with a rate constant in the range of 0.7-1.4 × 10^{-2} and 7.0-2.5 × 10^{-5} sec^{-1}.[213]



Scheme 8 Synthesis of alternating multiblock SHPs via bulk CuAAC click polymerization of A_2 and B_3 macromonomer.[214]

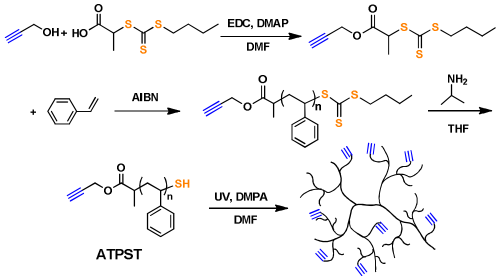
A_2 macromonomer + B_3 macromonomer approach was used to synthesize sequential multiblock SHPs (Scheme 8). A_2 macromonomer (**MM6**) was synthesized by esterification of PEG diols and carboxylic azide. B_3 macromonomer (**MM7**) was prepared via condensation between PCL triols and carboxylic alkyne. Through bulk click polymerization, the SHP with DP as high as 16 was achieved only in several minutes. The obtained amphiphilic SHPs showed two melting temperatures which belong to the PCL and PEG segments, respectively.[214]

4.2.2 Thiol-halogen substitutions

Macromonomers (**MM8**, PDI < 1.2) with dithiolbenzonate and bromoester groups were synthesized via RAFT polymerization.[215] Hexylamine was applied as both reduction agent and polymerization initiator, which can reduce tritrhiocarbonyl groups to thiols and catalyze thiol-bromo click chemistry simultaneously. The M_w of the resulted SHPs measured by static light scattering was 64,000 g mol^{-1} while it measured by GPC was only 30,000 g mol^{-1}. The difference of the M_w by different measurements indicates the obtained SHPs with the globular structure. The periphery of the resulted SHPs was covered with abundant bromo groups, which could be further modified via click chemistry.

4.2.3 Thiol-yne additions

The α-thiol-ω-alkynyl polystyrene (**MM9**) was formed via aminolysis of alkyne-terminated polystyrene trithiocarbonate (M_w = 787,000 g mol^{-1}, PDI = 1.07) in the presence of isopropyl amine. Thiol-yne click polymerization of **MM9** was initiated by 5 wt % DMPA (Scheme 9) under ultraviolet irradiation (λ = 365 nm). Within 180 min, 95% conversion was reached and the resulted hyperbranched polythioether had M_w of 42,000 g mol^{-1}.[216,217]



Scheme 9 Synthesis of HPs by the AB$_2$-type macromonomer, α-thiol-ω-alkynyl polystyrene (ATPST).

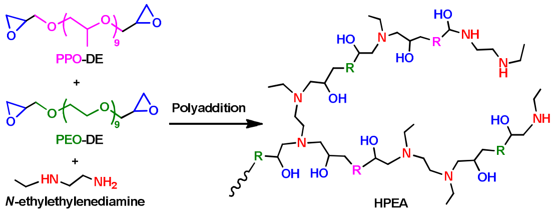
The macro-block-monomer alkyne dimethyl acrylamide-styrene thiol (ADMAST, **MM10**) was prepared via sequential RAFT polymerization of PYPBTC with dimethyl acrylamide and styrene, followed by aminolysis. The SHPs with M_w of 15,000 g mol^{-1} and PDI of 3.5 were synthesized using **MM10** as starting macromonomer.[208]

To synthesize ionized SHPs, alkyne *tert*-butyl acrylate-styrene thiol (A*t*BAST, **MM11**) was synthesized via sequential RAFT polymerization of *tert*-butyl acrylate and styrene and further aminolysis reaction. Thiol-yne click polymerization of **MM11**, followed by selective hydrolysis of *tert*-butyl ester groups affords SHPs with alternating poly(acrylic acid) and polystyrene blocks (M_w of 37,000 g mol^{-1} and PDI of 7.4). The PAA-PS SHPs showed a pH-dependance self-assembly in aqueous solution. The size of aggregates was 10 (in higher pH solution) and 500 nm (in lower pH solution), respectively.[217]

4.2.4 Epoxy-amine chemistry

Epoxy-amine adition reaction is another kind of click chemistry. The primary amine first undergoes an addition reaction with an epoxide group, generating a secondary amine which is able to take place the further addition reaction with second epoxide group.

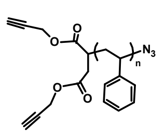
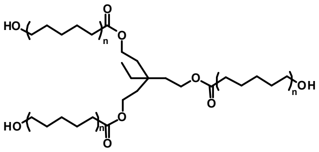
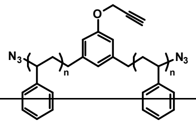
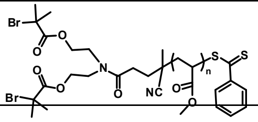
Jiang and Yin prepared a series of amphiphilic hyperbranched poly(ether amine)s (HPEAs) via epoxy-amine polymerization of B$_3$ monomer (*N*-ethylethylenediamine) with two kinds of A$_2$ monomers, poly(ethylene glycol) diglycidyl ether (PEO-DE, M_n = 526 g mol^{-1}) and poly(propylene glycol) diglycidyl ether (PPO-DE, M_n = 640 g mol^{-1}) (Scheme 10).[218] Changing the feed ratio, HPEAs were obtained with M_n of 10,000-18,000 g mol^{-1}, PDI of 1.3-2.2 and DB of 0.52-0.62. The resulted HPs are water-soluble and temperature-, pH-, and ionic strength-sensitive. Their cloud-point temperature could be adjusted from 35 °C to 100 °C by tuning the content of PEO moieties, pH values and ionic strength. Additionally, based on the resultant HPEAs, the subsequent modifications facilely afforded diverse novel materials.[219-221]

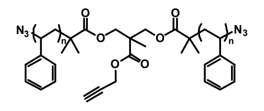
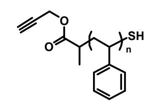
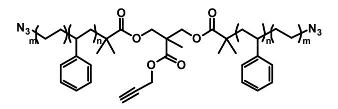
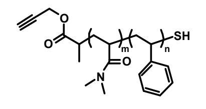
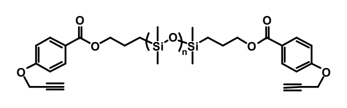
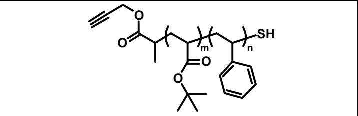
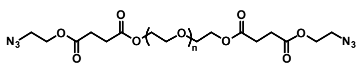
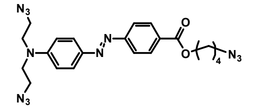


Scheme 10 Synthesis of HPEA via A$_2$+B$_3$ protocol following the mechainism of epoxy-amine click polymerization.[218]

Although various click reactions have been widely used for the synthesis of HPs, the employed monomers are usually not easily achieved and require several synthetic steps to prepare them. Development of novel synthetic strategies for monomers and HPs in a facile manner still is a very formidable task.

Table 4 Monomers and macromonomers for synthesis of SHPs.

	Structure	Type	Ref.		Structure	Type	Ref.
MM1		Y-type Macro AB$_2$ CuAAC	[209]	**MM7**		Macro B$_3$ CuAAC	[214]
MM2		Seesaw-type Macro AB$_2$ CuAAC	[210]	**MM8**		Masked Y-type Macro AB$_2$ Thiol-	[215]

						bromo	
MM3		Seesaw-type Macro AB_2 CuAAC	[211]	**MM9**		Y-type Macro AB_2 Thiol-yne	[216]
MM4		Seesaw-type Macro AB_2 CuAAC	[212]	**MM10**		Y-type Macro AB_2 Thiol-yne	[208]
MM5		Macro A_2 CuAAC	[213]	**MM11**		Y-type Macro AB_2 Thiol-yne	[217]
MM6		Macro A_2 CuAAC	[214]	**M34**		B_3 CuAAC	[213]

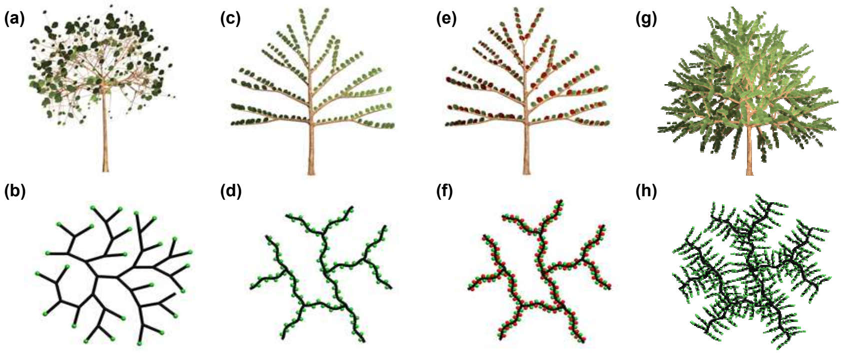


Fig. 9 (a) Densely branched tree. (b) CHP has high steric congestion that hinders post-functionalization in the core. (c) Sparsely branched tree. (d) SHP with the low steric congestion. (e) Sparsely branched tree with full scaffold leaves of different colors. (f) SHPs with full scaffold hetero functionality. (g) Sparsely branched tree with abundant side-branch on the scaffold. (h) Compact functional dendritic molecular brush (Reproduced from ref.s 222 and 223, with permission from Royal Society of Chemistry.)

5. Click post-functionalization

Besides development of synthesis, great progresses in the functionalization of HPs have been made. The modification of HPs is quite similar to the growth of leaves in a tree (Fig. 9). Functionalization of CHP only occured on the periphery, since its compact structure confined the external reactive molecules access and further modify (Fig. 9a and 9b). Just like densely branched trees mainly have their leaves grown on outer twigs, because their internal parts can receive few sunshine (Fig. 9e and 9f).[222,223]

In contrast, SHP has the sparse framework providing more convenience for subsequent functionalizations (Fig. 9c and 9d), which as the sparsely branched tree can grow leaves both at peripheral and in internal parts (Fig. 9g and 9h). As a result, it is possible to introduce full-backbone modification for SHP.

Apart from aforementioned click polymerizations for HPs, this versatile approach has been widely utilized to modify their periphery, core, both core and periphery. In this section, we mainly focus on click modifications of both CHPs and SHPs which were synthesized by non-click strategies (Fig. 10).

5.1 Functionalizations of the periphery

5.1.1 Functionalizations by CuAAC approach

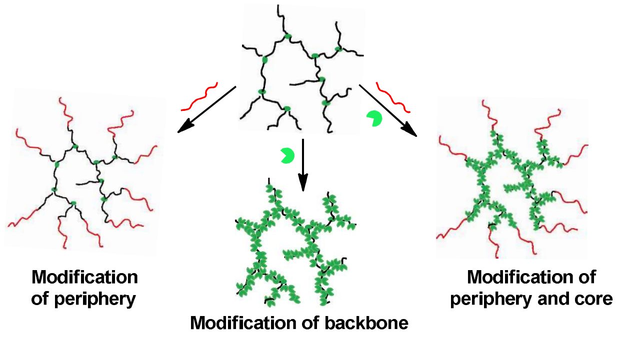


Fig. 10 Functionalizations of periphery, backbone and core as well as periphery of HPs.

Successful preparation of alkynyl- or azido-terminated HPs is the premise for further functionalization through CuAAC. Generally, the alkynyl group was introduced into HPs by the esterification of hydroxyl and alkynyl-containing acids in dichloromethane (DCM) or tetrahydrofuran (THF), while the azido group was achieved via the nucleophilic substitution of halogen and sodium azide in dimethyl formamide (DMF). Then, by CuACC modification, the resulted HPs possessed diverse specific functions.[224-231]

Alkynyl-terminated HPs were synthesized via the melt-transetherification polymerization of the hydrophobic **M35** and the hydrophilic **M36** (see Table 5). Afterwards, 1-

azidomethylpyrene was attached to achieve HPs, forming the fluorescent polyether via CuAAC chemistry.[224] The similar process for the polymerization of **M37** or **M38** was also reported.[225,226]

Alkynyl-ended core-shell type HPEs were made from **M39**.[227] Followed by CuAAC modification of azido-ended long alkyl chain and peripheral alkynyl groups, amphiphilic star-like brushes were achieved, which can be self-assembled into Janus structures in aqueous solution.

Azido-ended HPEs were prepared by carbodiimide reaction followed by the polyesterification of **M40**.[149] They were further modified into amphiphilic ones for loading small guest molecules. In addition, the PEG-*grafted*-hyperbranched cyclodextrin was also synthesized by CuAAC. It exhibited the interesting multi-guest encapsulation/release properties.

Voit *et al* ultilized the activator generated electron transfer (AGET) ATRP strategy synthesize HPs using **M41** as the inimer. Compared to the traditional ATRP, the AGET one can carry out under looser experimental conditions and greatly simplified the polymerization procedure. After the azidation, these abundant peripheral chloro groups were replaced by azido groups which further reacted with propargyl alcohol, resulted in the hydroxyl-terminal HPs.[228]

A new kind of HCPE with a long wave emitting property was synthesized using **M42** as reactant. The terminal amino groups introduced via CuAAC were further linked with anti-HER2 antibody.[229] The functionalized HCPE displayed the performance of targeted cellular imaging at low cytotoxicity and good photostability.

Via condensation reaction between the peripheral primary amino groups with 5-hexynoic acid or 10-undecynoic acid, two kinds of alkynyl-terminated HPEIs were synthesized. The mono-(6-azido-6-desoxy)-*b*-cyclodextrin (CD-N$_3$) was attached onto alkynyl-containing HPEIs, giving the HPEI-(CH$_2$)$_3$-CD and HPEI-(CH$_2$)$_8$-CD. Both of them showed the property of stimuli-responsive contraction and expansion.[230] Based on the host-guest interaction between adamantanes and cyclodextrins, two kinds of adamantly-containing anthraquinone dyes were used to further modify HPEIs. In water, the functionalized HPEI can form nanoparticles with the average diameter of 260 nm and the critical temperature of 26 °C.[231]

The (propargyl carbamate) ethyl disulfide ethyl 1-carbamide-imidazole (**S1**) or 3-azidopropyl ester of carbonylimidazole (**S2**) was applied to modify HPEI via conjugation between imidazole ring and primary amine. The subsequent click reaction between the obtained alkynyl- and azido-HPEIs generated the disulfide-containing HPEI nanoparticles, which were able to bind the plasmid DNA and showed a potential use for gene vector.[232]

Incidentally, by the SCROP approach, the achieved HPGs have been widely used in biochemistry and materials science, due to their high DB, inert polyether scaffolds and abundant hydroxyl groups. The alkynyl- or azido-terminated HPGs can be further modified via CuAAC.[233-241]

5.1.2 Functionalizations by thiol-ene addition

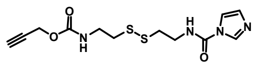
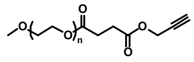
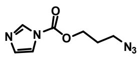
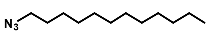
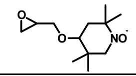
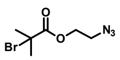
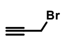
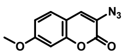
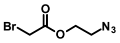
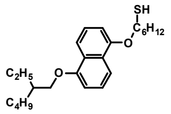
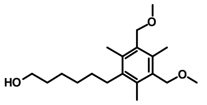
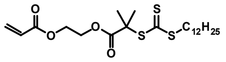
Both thiol-ene addition (between thiol and vinyl groups) triggered by free radical and thiol-Michael addition (between thiol and acrylate groups) activated by catalysts have been ultilized to modify the periphery of HPs. Etherification and esterification are often used for synthesis of unsaturated double bond- or thiol-terminated HPs or modifiers.

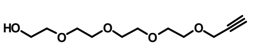
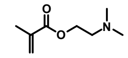
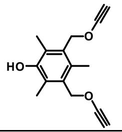
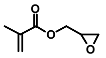
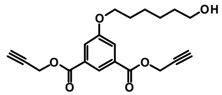
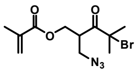
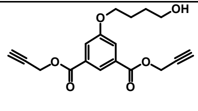
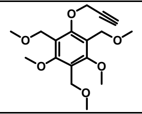
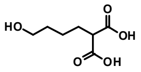
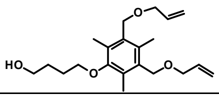
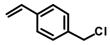
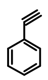
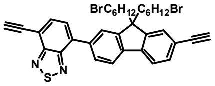
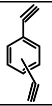
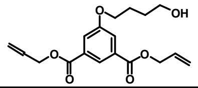
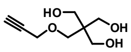
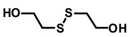
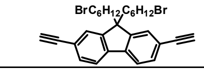
Alkene-terminal HP was made by melt-transetherification of **M43**. The HP could be further modified by benzylthiol, 2-mercaptoethanol, *N*-benzoyl cystine and hexadecyl thiol.[242]

Allyl-functional HPG was modified with monothiol-ended PEG by thiol-ene click chemistry to form HPG-*star*-PEG.[243] Via the copolymerziation of glycidol and 2,2'-dihydroxyethane disulfide (**M44**), followed by cleavage of the disulfide-containing HPG, the generated monothiol-functional HPG could be used for further modificaitons.[244]

Through thiol-Michael addition, thio-glucose was attached on peripheral vinyl groups of the hyperbranched poly (amine-ester), forming core-shell glycopolymers with the strong photoluminescence.[245]

Table 5 Click monomers for post-functionalizations.

	Structure	Type	Ref.		Structure	Type	Ref.
S1		CuAAC	[246]	**S6**		CuAAC	[49]
S2		CuAAC	[246]	**S7**		CuAAC	[49]
S3		Amine-epoxy	[261]	**S8**		CuAAC	[49]
S4		Menschutkin	[49]	**S9**		CuAAC	[228]
S5		Menschutkin	[49]	**S10**		Thiol-ene	[228]
M35		AB$_2$ Transetherification	[238]	**M45**		Inimer RAFT-SCVP	[49]

M36		AR Tansetherification	[238]	**M46**		Vinyl monomer RAFT-SCVP	[49]
M37		AB_2 Transetherification	[239]	**M47**		Vinyl monomer RAFT-SCVP	[63]
M38		AB_2 Transesterification	[240]	**M48**		Inimer ATR-SCVP	[169]
M39		AB_2 Transesterification	[241]	**M49**		B_3 Transetherification	[228]
M40		AB_2 Esterification	[149]	**M50**		AB_2 Transetherification	[228]
M41		Inimer AGET ATR-SCVP	[242]	**M51**		A_1 & A_2 Chain-Growth Polymerization	[262]
M42		A_3-A_3 Polycyclotrimerization	[243]	**M52**		A_1 & A_2 Chain-Growth Polymerization	[262]
M43		AB_2 Transesterification	[256]	**M53**		B_3 (initiator) ROP	[263]
M44		B_2 (initiator) ROP	[258]	**M54**		A_3-A_3 Polycyclotrimerization	[243]

5.1.3 Functionalizations by aza-Michael addition

To obtain HPG with peripheral amino groups, Frey's group employed the three-step synthetic strategy.[246] Firstly, hydroxyl group was esterified with 4-tolunesulfonyl chloride, followed by the azidation to transform chlorine atoms into azido groups. Secondly, through the Staudinger reduction, azido groups were reduced into primary amines. Finally, by the aza-Michael addition between amine and *N*-isopropyl acrylamide, the resultant HP was endowed with thermosensitivity.

5.1.4 Functionalizations by amine-epoxy chemistry

Due to the presence of abundant amino functional groups, HPEIs could be directly modified via amine-epoxy reaction. For example, 4-glycidol-2,2,6,6-tetrametylpiperidin-1-oxyl **(S3)** was attached onto the periphery of HPEIs. Subsequent modifications of PEO and PS afforded the three-layer products. The onion-like HPs could simultaneously deliver both polar and apolar guests.[247]

5.2 Functionalizations of backbone

Besides the peripheral modification of HPs, their backbones also can be modified, affording various functions. For CHPs, the densely branched framework makes the functionalization of core very difficult. Only about 70% of reactive sites in the compact core could be functionalized.[222] On the contrary, the SHP possesses a sparser branching structure, giving a lower steric hindrance. Combined the loose backbone architechture with orthogonal click chemistries, diverse functional groups can be introduced into all scaffolds.

Gao *et al.* reported that as the bromine linked with strong electron-withdrawing group(s) such as carbonyl or sulfuryl group, the Menschutkin reaction between bromine and tertiary amino group can be quickly completed within several seconds at 0 °C, whereas, without electron-withdrawing group jointed to bromine, the addition reaction needs more than ten hours even under the heating condition.[223] Now, Menschutkin click reaction has been successfully employed in post-modification of tertiary amino group-containing SHPs. Various functional groups, including alkynyl, azido, carboxyl, hydroxyl, *etc.*, have been introduced into scaffolds of SHP with 100% conversion.[108,223]

The dimethyl amino group-containing SHP was facilely syntehsized via the SCVP of RAFT inimer (**M45**) and **M46** in one-step.[108] As declared by kinetics study, both segments have dispersed regularly in the HP backbone. Dimethyl amino groups were fully reacted with propargyl bromide (**S4**) or azido bromide (**S5**) by Menschutkin click chemistry, forming the clickable SHPs (Fig. 11 and 12).[108,223]

Besides, azido-functional SHP was conjugated with **S6**, affording a hydrophilic dendritic molecular brush. Alkynyl SHP clicked with **S7** or azido ATRP initiator (**S8**), affording amphiphilic hyperbranched polyelectrolyte or ATRP macroinitiator.[108]

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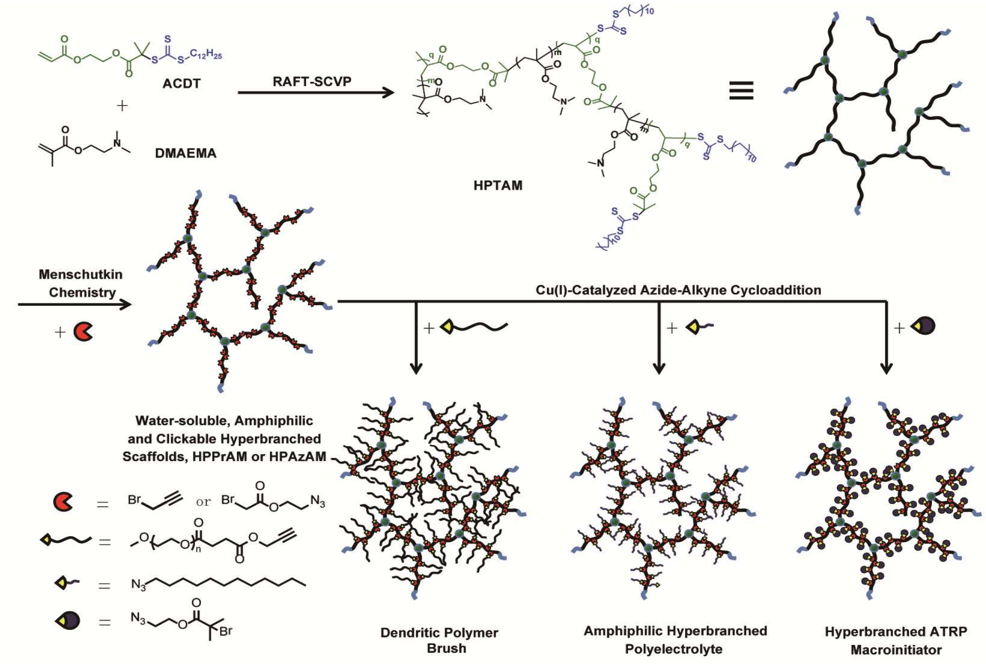

Fig. 11 Synthesis of dimethyl amino SHPs and subsequent click functionalization (Reproduced from ref. 108, with permission from American Chemical Society).

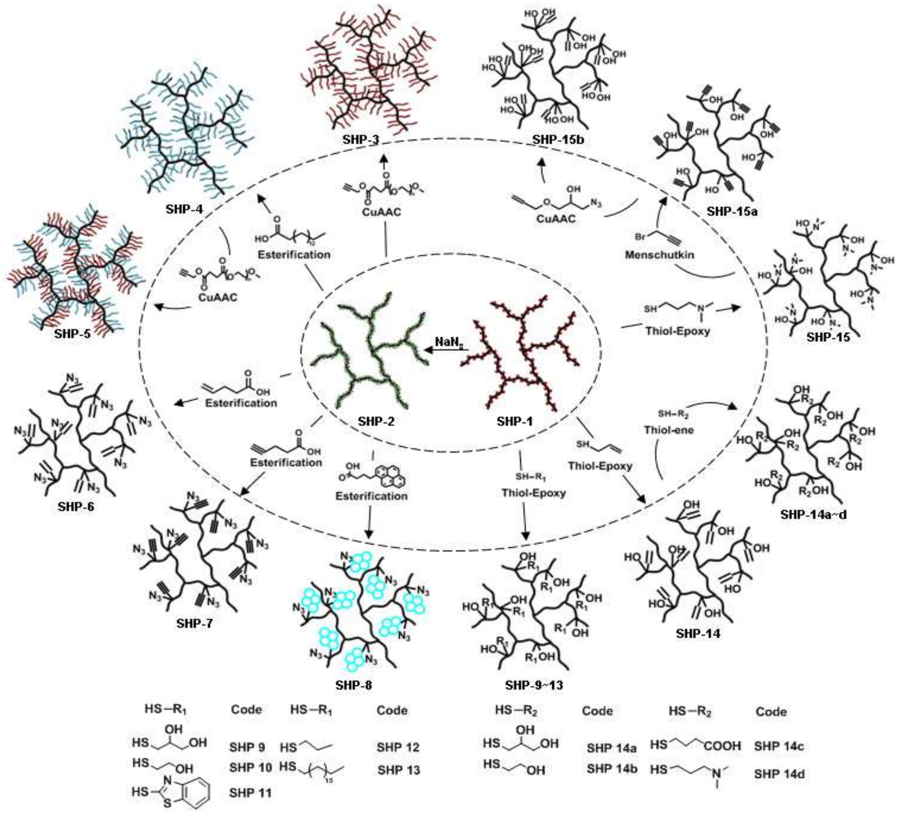

Fig. 12 Hetero functional group engineering of SHPs via click chemistry. (Reproduced from ref. 223, with permission from Royal Society of Chemistry.)

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ARTICLE TYPE

The RAFT-SCVP approach realized whole-scaffold epoxy groups via copolymerization between inimer **M45** and **M47**.[222] Since the epoxy ring is highly reactive under attack of strong nucleophiles, sodium azide, giving the SHPs with hetero functionality of hydroxyl+azide (Fig. 11).[108] Subsequent click functionalization via a collection of click chemistries, including thiol-ene, CuAAC and Menschutkin quaternarization click chemistries, afforded SHPs with hetero-functionality of hydroxyl+alkene/carboxyl/alkyne/tertiary amine, dual/triple hydroxyl, alkene/alkyne+azide, dual hydroxyl+alkene, *etc.*, all at ~100 % conversion (Fig. 12).[223]

5.3 Functionalizations of periphery and backbone

For more complexed architechures and functions, both the core and periphery of HPs can be modified. As shown in Fig. 13, a clickable inimer-containing HP was synthesized through SCVP using the 3-azido-2-(2-bromo-2-methylpropanoyloxy) propyl methacrylate (**M48**) as the starting material.[248] The pendant bromo and azido groups were used to initiate the second ATRP of MMA and the click reaction with the mono-alkynyl PEG (**S6**) chains in one-pot, respectively. The obtained HPs with the multihetero-arm displayed a unique dynamic self-assembly behavior.

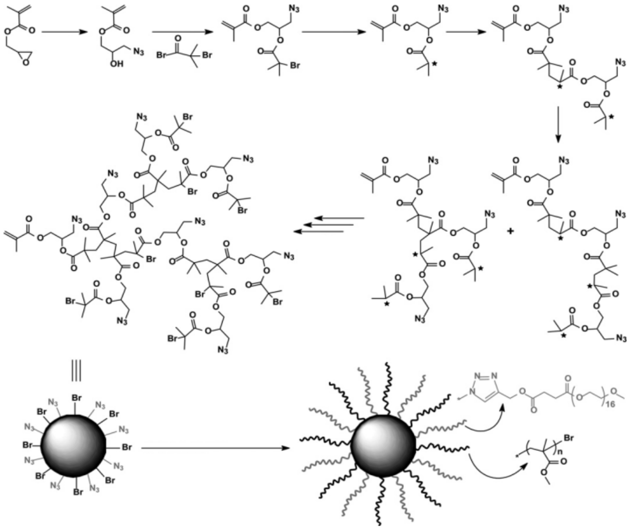


Fig. 13 Clickable hyperbranched polymer synthesized from SCVP. (Reproduced from ref. 248, with permission from Royal Society of Chemistry.)

Based on the difference between methoxy groups of **M49** and allyloxy groups of **M50**, it resulted in the clickable HPs with an alkynyl core and allyl shell.[249] Via CuAAC chemistry, the core was conjugated with an azido acceptor molecule **S9**. The allyl shell was modified by a thiol donor molecule **S10** through thiol-ene addition.[249] Carrying two different kinds of chromophores, the hetero-functional platform showed the fluorescence resonance energy transfer (FRET) from periphery to core.

5.4 Functionalizations of core

Incorporation of clickable groups into the core of star-like HPs, subsequent modifications can be carried out smoothly via click reactions. Here, DMF is a very suitable solvent, due to its good chemical stability, high dissolving capacity, and moderate polarity.

Copolymerization of mono-alkynyl monomer (**M51**) or diyne monomer (**M52**) for HPs was reported using a cationic diphosphine-ligated Pd (II) as catalyst. The residual alkynyls were dispersed randomly in the whole scaffold, yielding clickable HPs. Mono-azido polystyrene was clicked onto the triple bond via CuAAC, forming the star-like polymer with a core-shell structure.[250]

Using propargyl alcohol or **M53** as the initiator, alkynyl-functional HPG with moderate M_w was synthesized via SCROP.[251] The azido-biotin, -fluorophore or -amine has been used to functionalize the alkynyl-ended HPG, expanding its application fields.[252]

By alkynyl polycyclotrimerization of **M54** and subsequent CuAAC modification, fluorescent hyperbranched conjugated polyelectrolyte (HCPE) was synthesized.[229] The core of HCPE was ionized via the addition of bromo and triethylamine. With peripheral PEG brushes, the HCPE showed a double-layered ingredient structure and good water-solublility, which could be ultilized for breast cancer cell imaging.

Compared with CuAAC modifications, the Menschutkin reaction can give rise to a water soluble quaternary ammonium salt core for polymer coloring or other specific applications (such as biomedicine). The tertiary amine-containing core was reacted with methyl iodide or propargyl bromide, affording amphiphilic HPs for coloring common polymers.[253-258]

6. Potential applications of HPs

HPs display such features as highly reactive groups, few chain entanglements, low or no crystallization, and so on, which endow them large free volum, tailor-made properties, high solubility in solvents, low viscosity, *etc*. Therefore, they have been utilized in fields ranging from photoelectric materials, nanotechnology, biomedicine, composites, coatings, adhesives, modifiers, and so forth (Fig. 14). However, most of them remain theoretical, only a few of HPs are actual products, such as, Boltorn$^{\text{TM}}$ (HPE, Perstorp Co., Sweden) and Lupasol$^{®}$ (hyperbranched polyethylenimine, BASF Co., Germany).

6.1 Conjugated HPs

Compared to linear counterparts, hyperbranched conjugated polymers (HCPs) have better solubility and processibility. Moreover, their highly branched and globular frameworks can prevent aggregation and reduce interchain actions. Therefore, HCPs are promising for photoelectric materials.

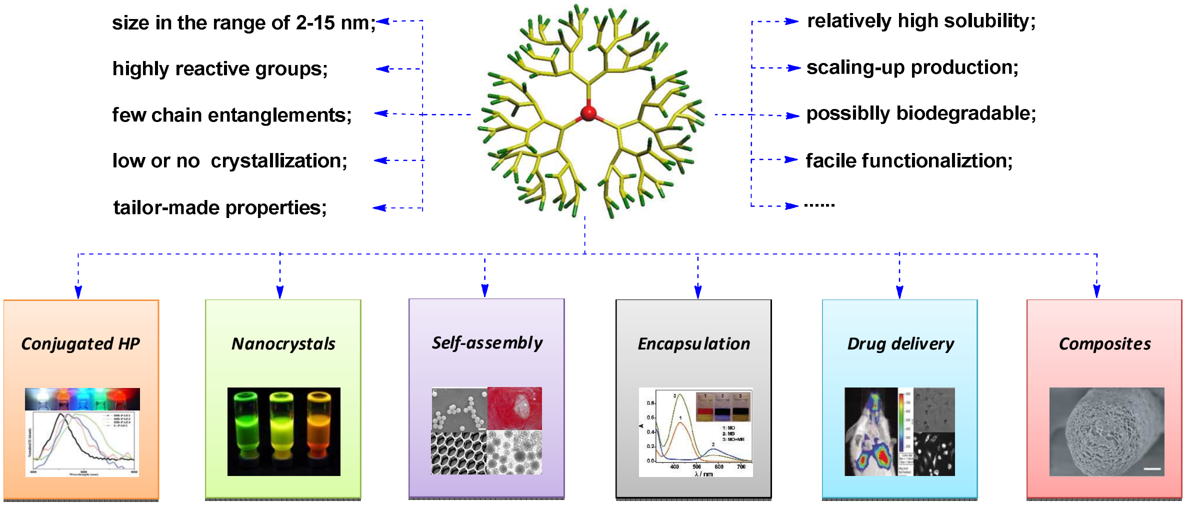


Fig. 14 Relationship between structure and property of HPs and their major applications.

6.1.1 Light-emitting materials

Driven by the requirement of unusual properties, many efforts have been devoted to design and synthesize HCPs in recent years. Among diverse HCPs, polyfluorines (PFs) are very important candidates for blue light-emitting diodes (LEDs) because of their desirable luminous intensity.[259-266] To reduce detrimental green emission and/or inherent ketonic defects, incorporation of triazole,[260] truxene,[261,262] oxadiazole,[264,265] or carbazole[266] building units into HPFs has improved their electron transport abilities.

Through Suzuki cross coupling, a series of novel HPFs had been prepared with M_n of 5,500-9,700 g mol^{-1} and PDI of 1.86-4.45.[261] The products were soluble in common organic solvents, such as, $CHCl_3$, CH_2Cl_2, and toluene, and displayed good thermal stability (T_d > 446 °C). Either in film or in chloroform solution, they exhibited absorption maxima at 349-378 nm. For the LED with HPF as the emitting layer, blue emission was up to 212 cd m^{-2} at about 19 V.

With hexaphenylbenzene as the core and 1, 3, 4-oxadiazole as adjusted units, the obtained HCP acted as the active layer in a two-layer PLED.[265] It showed a maximum luminous efficiency of 0.72 cd A^{-1} and the brightness of 549 cd m^{-2} at 16.5 V.

To improve the device efficiency, a new hyperbranched copper phthalocyanine (HCuPc) was synthesized by self-condensation of 4,4'-oxybis(phthalonitrile).[267] Here, HCuPc was used as a hole injection layer to replace commercially available PEDOT/PSS. Compared to the traditional PEDOT/PSS, HCuPc as a hole injection layer achieved a higher luminous efficiency (1.92 cd A^{-1}) and brightness (13,000 cd m^{-2}). Furthermore, the organic solvent-soluble HCuPcs enable the fabrication of high quality PLEDs.

6.1.2 Non-linear optical materials

With donor-π-acceptor chromophores, NLO materials play a significant role in latent electro-optic applications.[268] For high performance NLO materials, one of the daunting problems is how to eliminate intermolecular dipole-dipole interactions. Such defects can be efficiently restrained by building chromophores as main-chain,[269,270] side-chain [271,272] and periphery [273] of HPs.

To prevent undesired dipole-dipole interaction, direct polycondensation via A_2+B_4 route afforded the soluble HPs with isolation chromophores.[269] As declared by second harmonic generation measurements, the d_{33} coefficients were 40.0 and 73.6 pm V^{-1} with Φ values of 0.11 and 0.13. Peripheral modified HPs by chromophore can also reduce dipole-dipole interactions. Although the chromophore content (about 20-23 wt %) is lower than those of linear counterparts, d_{33} coefficients are similar (up to 65 pm V^{-1}), which is attributed to their unique molecular architectures.[274]

Rigid groups, such as three triazole ring formed by click reaction, can effectively reduce molecular interchain aggregations. Azo-chromophore-containing HP was synthesized via click chemistry using AB_2 type monomers.[156, 177] Detected by the second harmonic generation, the resulting d_{33} coefficients of them were 77.9 and 124.4 pm V^{-1}, which are ascribed to the suppressed electric static interactions of chromophore moieties caused by rigid triazole rings.

Besides, via chemosynthesis, high performance NLO materials can also be achieved by a macromolecular dopant strategy.[275] A hyperbranched NLO oligomer (o-HP) (M_n of 3,300 g mol^{-1}) was synthesized and further used as a dopant agent. The o-HP could be soluble in aprotic solvents such as DMF and NMP. As the specimen contained 15 wt % of o-HP, the d_{33} reached 65 pm V^{-1}.[276]

6.2 HP-stabilized nanocrystals

Nanocrystals (NCs) include insulator, semiconductior and metal crystals. They exhibit unique size-dependent physical or chemical properties.[277,278] Spontaneous aggregation among NC particles leads to the performance degradation. To restrain it, HPs are often used as the stabilizer for preparation of NCs because of their specific three-dimensional structure, good solubility, and a lot of intramolecular cavities. The influence of HP architecture on the synthesis of NCs majorly shows as the following three aspects: i) their unique 3D structure can provide sufficient hindrance and efficiently suppress the tendency of aggregation; ii) plenty of cavities in HP templates confining the free diffusion of NCs' precursors, it is useful to control the size of NCs; and iii) the terminal groups endow the HPs enough functionalized flexibility, facilitating the synthesis and the size control of NCs.

Based on the synthesis process of NCs, three approaches have been developed: i) HPs first, using HPs as stabilizers to directly prepare NCs, ii) ligand-exchange, achieving NCs with surfactants or linear polymers as ligands, followed by ligand replacing step with appropriate HPs, and iii) grafting or *in situ* growth of HPs from the surfaces of premade NCs (Fig. 15).

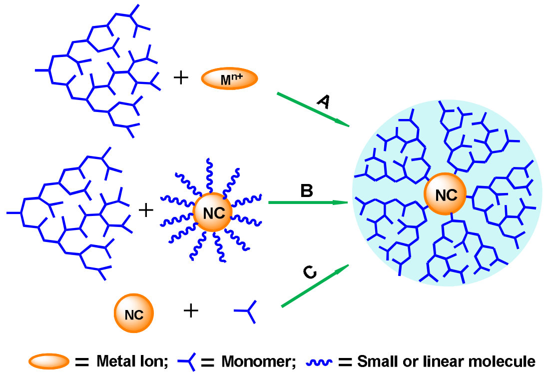


Fig. 15 Three methods for the synthesis of NCs: A “HPs first”, B “ligand exchange” and C “NCs first”.

Up to now, six major kinds of HPs were employed to prepare NCs, such as HPAMAM[279-284], HPEI[285-295], HPG[296-305], HPE[306-309], HPAM[310-312] and HPEO[313] (Fig. 16). Using these HPs as stabilizers, a lot of semiconducting and metal NCs have been prepared for the diverse applications.

6.2.1 Semiconducting nanocrystals

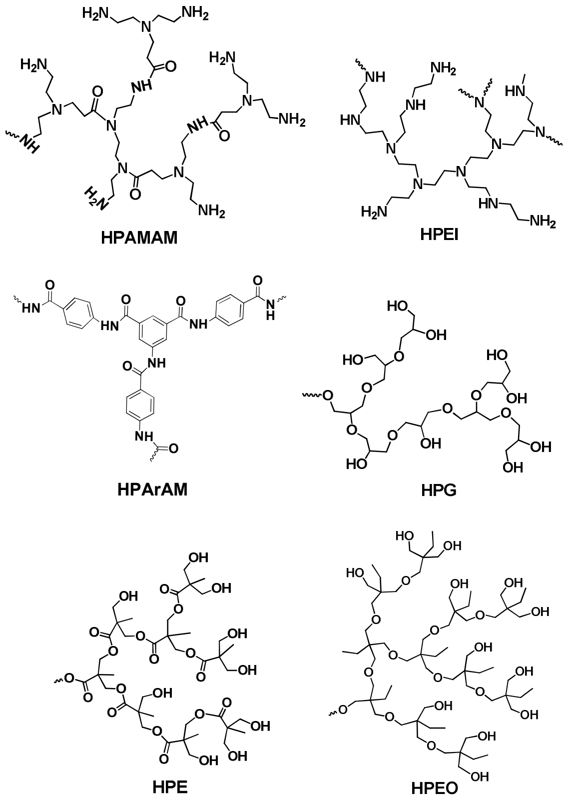


Fig. 16 Schematic structures of classic HPs used as stabilizers to prepare NCs.

Except NLO materials, semiconductor NCs, also called as quantum dots (QDs), have been used in optical devices, biosensors, and biological imaging, *etc*. Compared with those organic materials, QDs have better thermostability and longer service life.

Most of the QDs were synthesized by HPs first strategy (Fig 15A).[279-293, 295-297] Hydroxyl-ended HPG (M_n > 20,000 g mol^{-1}) was directly used as the stabilizer to prepare QDs (Fig. 17). The obtained QDs include ZnS, Ag_2S, PbS, CuS and CdS.[298] Due to the role of HPG, various QDs displayed good solubility in water and DMF. Moreover, the QDs showed low toxicity and good biocompatibility. Except unmodified HPGs, thioether-functionalized HPGs could be employed to prepare CdS and CdSe QDs.[299] Interestingly, the sizes of the resultant QDs depended on the molecular weights of the modified HPGs.

Compared to HPs first method, the ligand-exchange strategy shows its superiority in size control of NCs since the used NCs can be pre-prepared. HPEI (M_ws of 800 and 25,000 g mol^{-1}) exchanged with hydrophobic surfactants of CdSe@ZnS QDs and formed a very stable colloid in chloroform.[296] Followed the extraction of QDs from the non-polar solution with water, the HPEI-coated CdSe@ZnS with average diameters of 10.7 ± 1.4 and 17.5 ± 2.5 nm were afforded, respectively.

PEG grafted HPEI (PEI-*g*-PEG) (M_n = 18,500 g mol^{-1}) was utilized to load and stabilize CdSe/CdS/ZnS QDs (6.5 nm in diameter) via ligand-exchange strategy.[314] The grafted PEG segment is crucial for reducing the cytotoxicity of PEI and for improving the stability of QDs.

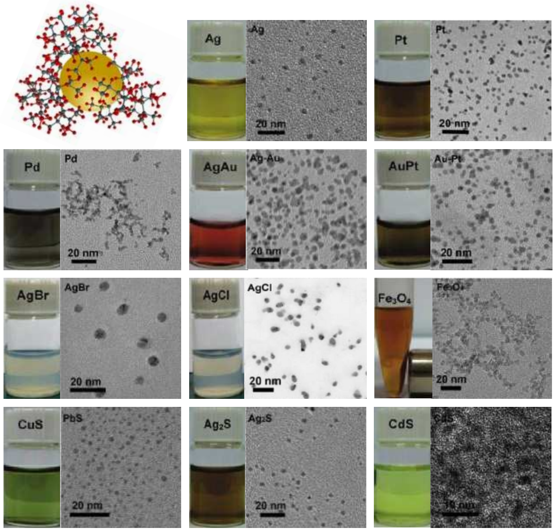


Fig. 17 Photographs of the aqueous solutions (left) and TEM images of HPG-stabilized nanocrystals (right). (Reproduced from ref. 298, with permission from American Chemical Society).

Compared with aforementioned approaches, surface chemical grafting on QDs is a more reliable way to stabilize NCs. Coating the QD with a protecting shell can effectively avoid fluorescence quenching or toxic metal ions releasing. [295,302,303, 315-321]

Up to now, several kinds of HPs including HPG,[319,320,324] PDMAEMA,[320] HPEI,[306,307] *etc.*, have been successfully grafted from the surfaces of preformed QDs. HPG-stabilized CdTe QDs were prepared by *in situ* surface-initiated ROP of glycidol. Compared to unmodified ones, the biocompatibility and stability of CdTe@HPGs were notably improved due to the HPG cladding layer.[318]

Multicarboxylic HPG-grafted $SiO_2@Fe_3O_4$ magnetic hybrids were synthesized and used for the growth of various noble NCs such as Pt, Au, and Pd (with the average sizes of 4.8±0.5, 6.0±0.6, and 4.0±0.4 nm, respectively) (Fig. 18).[319] Their loading capacities of 0.296, 0.243 and 0.268 mmol g^{-1} were obtained, respectively, due to the amplification effect of HPG. Besides, these noble NCs could catalyze the reduction reactions of 4-nitrophenol, alcohol oxidation, and Heck reaction with the high catalytic activity and good reuse property. HPG-stablized multifunctional magnetic hybrids possessed promising potential applications in catalysis and biomaterial areas.

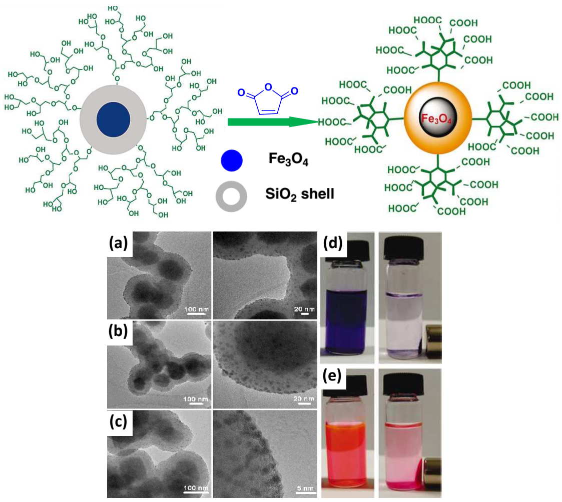


Fig. 18 Preparation of NCs supported on HPG-functionalized magnetic hybrids (top); TEM images of Pt (a), Au (b), and Pd (c) nanoparticles on the $(HPG\text{-}COOH@SiO_2)@Fe_3O_4$ supports; and their applications for dyes-loading (d and e). (Reproduced from ref. 319, with permission from American Chemical Society).

6.2.2 Metal nanocrystals

Similar to the synthesis of QDs, stable metal NCs can be prepared under the assistance of HPs. Among the numerous available HPs, amine- or sulfur-containing HPs are widely used due to their stronger interaction with metal NCs.[320-325] Based on specific properties of metallic elements themselves, the corresponding metal NCs have been widely used as catalysts,[320-323] disinfections,[324] sensors,[325,326] and so on. Without the undesired aggregation, they exhibited high catalytic activity and good reusable property.

Ni NCs were facilely prepared using HPAMAM grafted polyvinylamine (PVAm)/SBA-15 as a stabilizer.[320] The resulted Ni@PAMAM-PVAm/SBA-15 NCs showed the high catalytic efficiency in reduction of aromatic nitro compounds. Compared to PVAm/SBA-15, it could cut reaction time in half. In addition, Ni NCs could be reused ten times without obviously loss of activity.

Surface modified polyacrylonitrile fiber (PANF) by HPEI was applied as *in situ* supporter to prepare Au NCs (3.0 nm in diameter).[321] The resulted Au@PANF-*g*-HPEI NC was efficient heterogeneous catalyst for reduction of 4-nitrophenol by $NaBH_4$. Interestingly, the Au@PANF-*g*-HPEI with lower HPEI content performed better in catalytic rate, and recovered as well as reused times.

Hyperbranched polylysine reacted with stearoyl/palmitoyl chloride and glycidyl hexadecyl ether, respectively, affording amphiphilic HPs. Using the resultant HPs with M_n of 9,400-10,700 g mol^{-1} and DB of 0.50-0.54 as templates, various stable monometallic (Ag, Au, and Pd) NCs (about 5 nm in diameter) were synthesized in organic solvents for versatile applications.[322]

Silver NCs were prepared using hyperbranched polyamine as the stabilizer via the reduction. As declared by biological activity detections, silver NCs exhibited good antibacterial activity against *B. subtilis* and *S. aureus* bacteria.[324] An interesting phenomenon is that the branching architectures of HPs have an effect on the antimicrobial activity.[327]

Water insoluble HPC was synthesized via ATRP-SCVP of styrene and *p*-chloromethyl styrene.[328] HPC was further utilized as *in situ* template for preparation of Ag NCs. The Ag@HPC NC (around 4-5 nm in diameter) exhibits excellent dispersion and stability (in the absence of aggregation even standing for 6 months). It would be a promising electrochemical sensor because of the good catalytic activity for the reduction of H_2O_2.

Self-assembled aggregations of HPs have been applied as stabilizers for NCs.[329-331] Hyperbranched poly(ethylene glycol) monomethylether methacrylate (HPEGMA) was used to synthesize Au@HPEGMA NCs via the ligands exchange approach.[332] Combining different Raman tag molecules with hybrid complexes would be used as various surface enhanced Raman scattering diagnostic probes for nanomedicine application.

Incidentally, the DB of HP[328], reactive temperature[331] and concentration of matel ion[331,332] have an effect on the particle size of NCs. Except monometallic (Au, Ag, Pt, Pd, and Ru) NCs, bimetallic (Au/Pt, Au/Pd, and Au/Ru) NCs[323] and smart HP-stabilized NCs[246] (thermo- or pH-responsive one) have also been easily achieved by the similar strategy.

6.3 HP-based supramolecular self-assembly

6.3.1 Self-assembly of amphiphilic HPs

Molecular self-assembly is a common phenomennon in nature. With the regular molecular structure, surfactants, linear block copolymers and dendrimers can self-assemble into well-organized supramolecular objects.[333,334] However, the mystery of self-assembly of HPs has not been unveiled until 2004.[335] The self-assembly of HPs was ignored for a long time because of their irregular molecular structures. If strong interaction originates from hydrogen bonding, electrostatic attraction, or host-guest self-recognition can surpassed the effect of molecular structure, the self-assembly of HPs will be a spontaneous process.

As shown in Fig. 19, various morphologies were formed by self-assembly of HPs, including micells (0D),[335-352] fibers or tubes (1D),[335,352-359] vesicles or films (2D)[360-367] and networks (3D)[368,369]. Interestingly, the HP with the similar architecture can self-assemble into entirely different topologies of nano-objects. For instance, the HPG-*star*-linear polymers with the same core (HPG) and different peripheral linear polymer segments (such as, PEO[334], PPO[342], PMDETA[344], *etc.*) will self-assemble into diverse nanoparticles, from micells to vesicles (0D~3D) (Fig. 19). Today, self-assembly of HPs has been a research focus, due to the developed synthetic methodology and their promising potential applications.

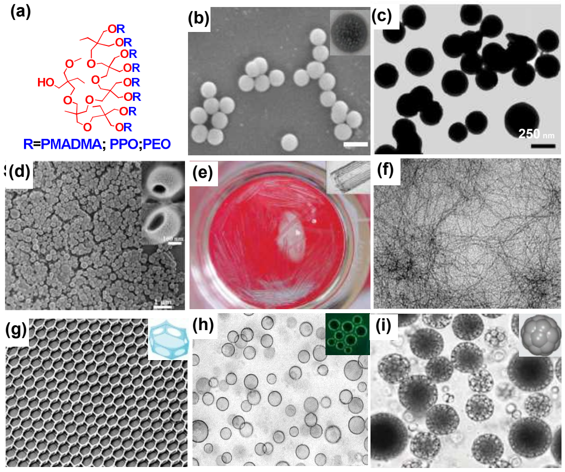


Fig. 19 Various self-assembled structures from 0 to 3D by the HPs (a). 0D (b-d), 1D (e, f), 2D (g), and 3D (h and i).

With more complicated structures (such as alternating multiblock copolymers[214], miktoarm polymer brushes[370], *etc.*), amphiphilic hyperbranched copolymers (AHPs) were synthesized. Based on the results of AFM and DLS measurements, their self-assembled morphologies mainly depend on M_n (or volume fraction) of block moieties, type of solvent, and concentration of AHP.[214,370]

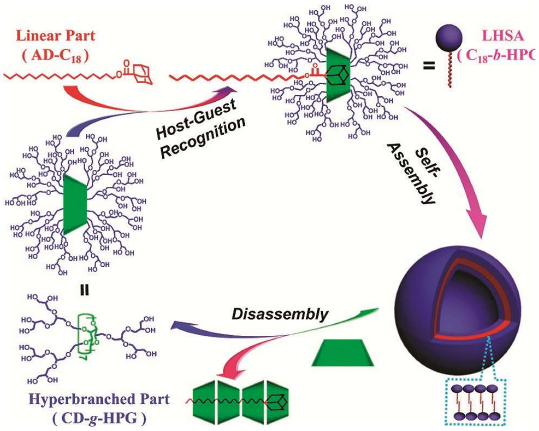


Fig. 20 Preparation, self-assembly, and disassembly progress of C_{18}-*b*-HPG. (Reproduced from ref. 375 with permission from American Chemical Society).

More recently, the supramolecular self-assembly utilizing host-guest molecular recognition interactions as driving force attracts increasing attentions.[371-376] Adamantine and β-cyclodextrin (β-CD)[371-374] as well as azobenzene and α-CD[375,376] are the frequently used host-guest molecular pairs. The self-assembly of HPG-azo and α-CD immediately occurs once addition of water into DMF solution. As demonstrated by AFM measurements, the complex showed a rod-like large micelle (about 540 nm in length and 127 nm in width). Irradiated by UV light at 365 nm for 30 min, the formed complexes collapsed and the cloudy dispersion became transparent again. Continuous stirring for 24 h in dark, rod-like micelles come into being appeared again. Switched by UV light irradiation, this “smart” reversible assembly and disassembly transitions would have wide potential applications.[375-379]

Just recently, the self-assembly of Janus HPs was develop by Zhou and Yan by the noncovalent coupling of the azobenzene and the hyperbranched polyglycerol grafted β-CD (β-CD-*g*-HPG). The Janus supramolecular object can be disassembled through UV light (λ= 365 nm) irradiation.[376]

Self-assembly of the hydrophobic adamantane-ended long alkyl chain and hydrophilic β-CD-*g*-HPG was carried out through adamantine (AD)/cyclodextrin (CD) host-guest interactions. The unilamellar vesicles self-assembled by C_n-*b*-HPGs (n= 12, 18 and 30) with excellent ductility that could be readily disassembled via the competitive host of β-CD (Fig. 20).[375]

6.3.2 Self-assembly of HPs for biomedical applications

Up to now, supramolecular complexes have displayed potential applications in biomedical areas because of their biocompatibility and devisable molecular architectures. Hyperbranched polyethers, polyesters, polyphosphates and polysaccharides can be used as candidates for cytomimetic chemistry, drug delivery, gene transfection, antimicrobial material, and bioimaging field.[26,34,380]

Compared with small molecular liposomes, the formed HP vesicles (HPVs) displayed lower membrane fluidity and higher stability. HPVs can form multivalent interactions among vesicles like the biomembrane does. Moreover, the size of HPVs is very close to that of the cell, allowing directly observes through the optical or fluorescent microscopy. In 2005, Zhou and Yan revealed membrane fusions initiated only by small perturbations or changing the osmotic pressure.[381,382]

Apart from cytomimetic chemistry, supramolecular aggregates formed by HP self-assembly have been utilized to load drugs. Compared with naked drugs, HP-drug complexes can improve solubility and prolong service time. Meanwhile, they can easily penetrate cell membranes and selectively accumulate as well as retain at tumor sites.[33]

Recently, a diselenide-containing amphiphilic hyperbranched phosphate (AHPP) (M_w = 6100 g mol^{-1} and PDI = 1.7) was synthesized.[383] Diselenide segments in the backbone structure of AHPP endowed it with the inhibiting the proliferation of cancer cell. In water, the AHPP could self-assemble into nanomicelles (aroud 50 nm in diameter) and could further encapsulate doxorubicin for combining therapy.

Haag and co-workers developed a series of HPGs for biomedicine applications via conjugated drug molecules, supramolecular encapsulation, and formation of microgel.[383-385]

Additionally, HP-fluorescent dye complexes, multiple functional HPAMAMs and HCPEs were able to form the stable nanomicelles for bioimaging.[385-388]

6.3.3 Supramolecular encapsulation for dyes

Due to the unique branched structure and numerous binding sites, amphiphilic HPs (AHPs) have been applied as hosts to encapsulate small molecule guests.[389-395] The loading capability (C_{load}) of AHPs is one of the most important parameters, which majorly depends on the following four factors: i) molecular weight and DB of the core, ii) shell density, iii) polarity gradient between core and shell, and iv) the affinity between core and guest molecules. Although supramolecular encapsulation has been successfully used in many fields such as phase-transfer, bioimaging, *etc.*, here, we mainly focus on the encapsulation of organic dyes and their further applications for polymer coloring.

In nature, the encapsulation of dyes by AHPs is a phase-transfer process, caused by self-aggragation behavior of AHPs in solution. Two kinds of micelles, micelle and inverse micelle, are involved in. In polar solvents, the micelle composed by hydrophobic core and hydrophilic shell is capable to encapsulate nonpolar dyes. On the contrary, in nonpolar solvents, the inverse micelle consisted of hydrophilic core and hydrophobic shell can encapsulate polar dye molecules.

Extraction technique was the common way for encapsulation of dyes. Under mixing condition, dye molecules pass through the water-oil interface and enter internal cavities of AHPs. The polar HPs, such as HPG,[389-394] HPEI,[396-401] HPAMAM,[402-404] HPSA[403-405] and hyperbranched poly(ester amide)/poly(ester amine),[406,407] have been utilized as polar cores of AHPs for encapsulations.

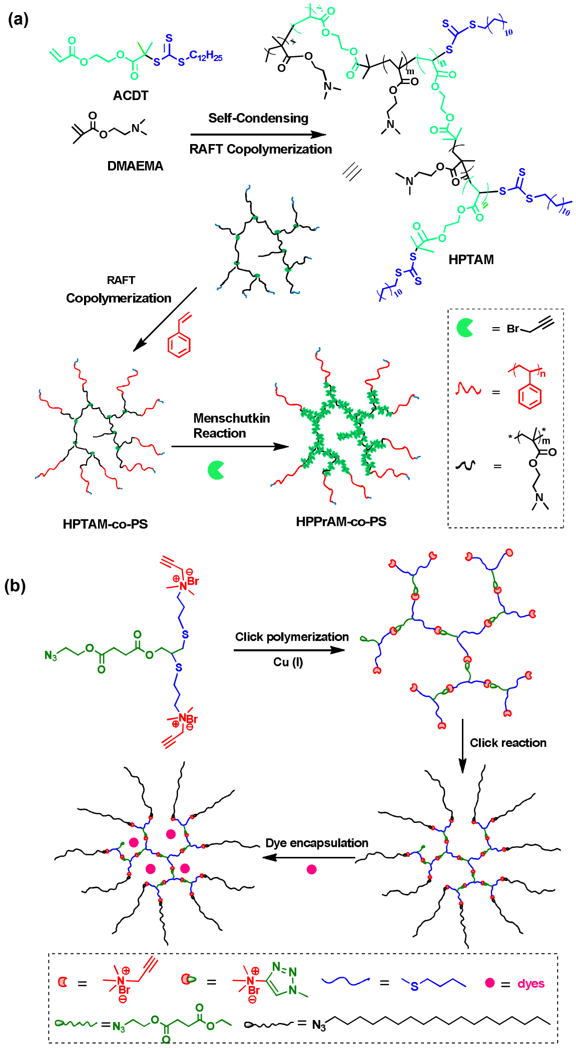


Fig. 21 Synthesis of HPTAM, HPTAM-*co*-PS and HPPrAM-*co*-PS *via* RAFT-SCVP and subsequent modification by Menschutkin reaction with propargyl bromide (a)[253] and synthesis of the amphihilic hyperbranched poly(quaternary ammonium salt) for dye-loading (b)[254].

Alkyl modified HPG was used as the host for encapsulation of water soluble dyes.[389] Congo red (CR) and Rose Bengal (RB) occurred irreversible transferring from aqueous solution into chloroform phase by extraction of the AHPG. However, the linear amphiphilic PGs did not work, owing to the lack of enough space. The result confirms that the highly branched structure is crucial during the encapsulation of dyes.[408,409]

Core-shell PEI-*star*-PLAs were synthesized by ring opening polymerization. It was found that C_{load} of dyes mainly depends on the length of PLA.[338] The longer arms lead to the higher C_{load}s, suggesting molecular weight of core or shell has an effect on the C_{load}.

In addition, increasing polarity difference between core and shell can also obtain high C_{load}. For the amphiphilic palmityl-functionalized HPSA, average C_{load}s of CR and MO are 41.8 and 19.4, respectively.[410] Valeryl- and nonanoyl-modified HPSAs with the lower polar difference displayed the lower C_{load}s.

Haag *et al.* reported that DB of AHPG had a significant effect on the C_{load} of dyes.[392,411] As DBs of AHPGs were in the range of 0.45-0.50, the highest C_{load} (about 3 mol $_{\text{dyes}}$ mol$^{-1}{}_{\text{AHPG}}$) was achieved. AHPG could only load anionic dyes, which was inoperative to cationic dyes, owing to the lack of strong enough core-dye interaction.

To confirm the importance of host-guest interaction on the C_{load}, partly[396] or completely[175,253] quaternized AHPs were used to encapsulate anionic dyes such as fluorescein sodium (FS), MO, CR, RB, *etc*. Hyperbranched poly(propargyl quaternary ammonium methacrylate)-*co*-polystyrene (HPPrAM-*co*-PS) was facilely prepared via RAFT-SCVP and Menschutkin reaction.[253] With a hydrophilic core and hydrophobic shell (Fig. 21a), the C_{load}s of HPPrAM-*co*-PS (M_n = 24,200 g mol^{-1}) achieved 24.1 of MO, 24.2 of RB, 238.4 of CR and 22.0 of FS.

Amphihilic hyperbranched poly(quaternary ammonium salt) (AHPQAS) was easily synthesized via successive click reactions (Fig. 21b). The resultant AHPs exhibit high C_{load}s of dyes and good dyeing property for general polymers (such as PMMA and SBS). The average numbers of dyes trapped in per AHPQAS reached 4.8 for RB, and 0.5-0.6 for MO, methyl violet (MV), FS and eosin Y (EY), respectively.[254] The polymer-dye complexes showed a good dyeing effect for PS or SBS. The color of the dyeing membrane was very stable and uniform. Similar results were also observed for amphiphilic POSSs.[175]

As declared by Frey *et al.*,[409] entrapped dyes could not escape from AHP-dye complexes unless the linkage connected the core and the shell was destroyed. So the dyes-containing complex exhibits sufficient stability and can further be applied to stain common plastics,[253-255] rubbers[253,254] and fibers.[256-258]

Long-alkyl-chain modified hyperbranched aromatic polyesters (HAPs) were used as nanocarriers to load organic dyes.[255] HAP-dye complexes could be monodisperse in the polyolefin matrix. The dyed polypropylene and high-density polyethylene displayed good coloring stability which was testified by extraction tests.

Inspired by Voit,[255] the alkyl chain-modified HPQA, Hybrane PS2550, was employed to improve the dyeing quality of PP fibres.[256] Additionally, by attaching HPAMAM to cotton fibres, the stain fastness and the levelling properties of the fibre were obviously improved.[257,258]

6.4 HPs for bioapplications

Chapter **6.3.2** has summarized the self-assembly of various AHPs for biomedical application. In this section, we will focus on the bioapplications based on their bulk properties, mainly including gene transfection, antibacterial/antifouling materials, bioimaging, and drug delivery. [333,412-433]

As cationic HPs, such as PEI, mixed with electronegative DNA, they can form HP-DNA polyplexes for gene transfection.

Comparing with viral vectors, HP-DNA polyplexes exhibited higher safety, weaker immune responses, more facile synthesis, and easier operation.[423-429]

Using natural molecule, kanamycin, as starting material, hyperbranched kanamycin-containing polymer (HPKM) was synthesized. In COS-7, the transfection activity of HPKM was up to 4.4×10^{8} RLU (mg protein)$^{-1}$, about 33-fold larger than that of chitosan. [423]

Furthermore, cationic long-chain HPEGs were applied for gene delivery.[426] As evidenced by fluorescence microscopic analysis, the polyplexe could efficiently penetrate into cells, due to its lower charge density. Besides, HPEHO-*g*-PDMAEMAs and PEI-*g*-HCPEs were also capable to improve gene transfection efficiency.[428,429]

Recently, HPs have also been widely used as antibacterial /antifouling materials. With good biocompatibility and chemical stability, HPGs are promising antifouling materials employed to prevent the attachment of proteins.[434]

Anchoring quaternary ammonium compounds (QACs) onto HPUA, the resulted shape-adaptive coating was capable to kill bacteria in a partially enveloping manner.[435] Since the adhesion force between *Staphylococcus epidermidis* and QACs was strong enough, these QACs could quickly remove membrane lipids and give rise to bacterial death. More than 99.99% of *Staphylococcus epidermidis* (1600 CFU cm^{-2}) could be killed by QACs. Notbly, its antimicrobial effect was persistent since QACs were directly connected with HPUA matrix by covalent bonds.

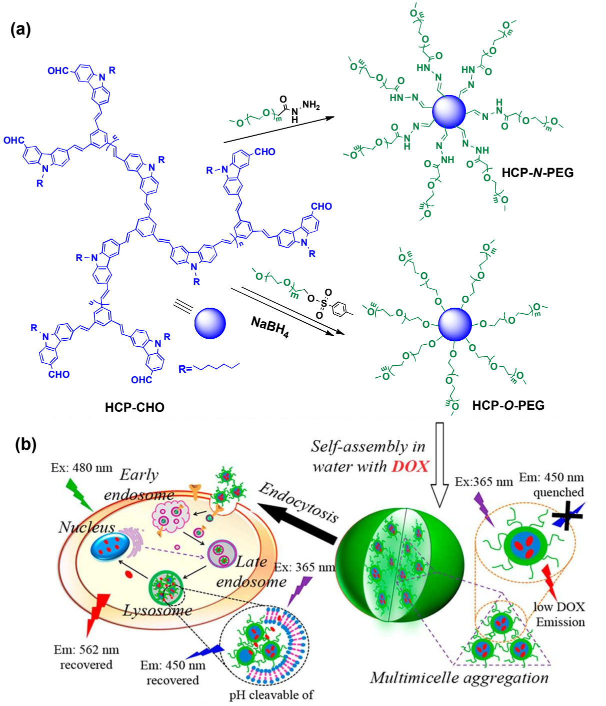


Fig. 22 Synthesis of HCP-*N*-PEG and HCP-*O*-PEG conjugated copolymers (a); self-assembly of conjugated copolymer and their endocytosis in the tumor cells (b). (Reproduced from ref. 438 with permission from American Chemical Society).

For bioimaging, HP-probe conjugates with the good water-solublility and available functional groups are good solutions to these problems, such as low quantum yield and poor specificity. Zhu and Yan grafted fluorescein isothiocyanate on the periphery of HPSA through the reaction of isothiocyanate and primary amino group.[436,437] With low cytotoxicity and good serum-compatibility, The HPSA-probe conjugate can be used for bioimaging or tracking cell.[428]

Star-like HPs, HCP-*N*-PEG and HCP-*O*-PEG, with a HCP core and linear PEG arms showed the superior fluorescein response sensitivity to those of small fluorophores and could be used as drug carriers for tumor therapy (Fig. 22 and 23).[438]

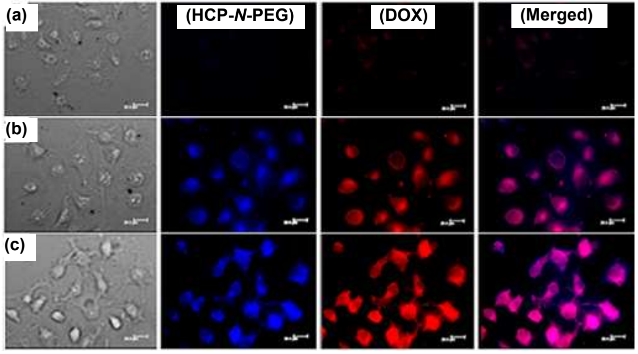
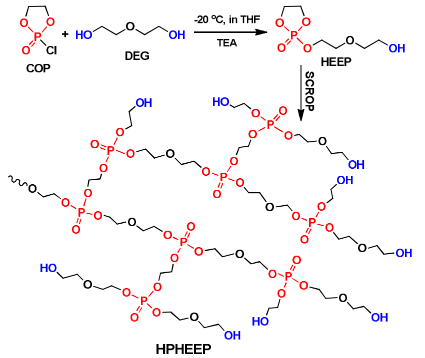
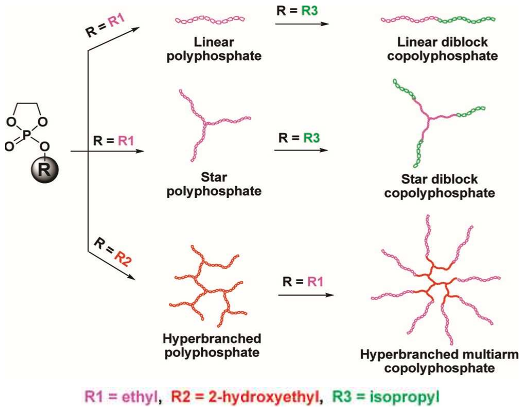


Fig. 23 Time-dependent fluorescence microscope images of of MCF-7 cells with the incubation time of 1(a row), 12 (b row) and 32 h (c row). (Reproduced from ref. 438 with permission from American Chemical Society).



Scheme 11 Syntheis of HPHEEP via the SCROP of HEEP.



Scheme 12 Selected topological structures of copolyphosphates. (Reproduced from ref. 440, with permission from American Chemical Society).

Degradable hyperbranched polyphosphates were developed by Huang and Yan via the SCROP of cyclic phosphate inimer, 2-(2-hydroxyethoxy)ethoxy-2-oxo-1,3,2-dioxaphospholane (HEEP), at 60 ^{o}C×14 h in bulk without any catalyst (Scheme 11).[439] The resultant HPHEEP with M_w of 5200 g mol^{-1}, PDI of 1.75 (GPC) and DB of 0.47 (on the basis of ^{31}P NMR measurements) was the promising biomaterial, due to no heavy metal pollution involved in it.

In addition, through sequential feeding strategy, a series of biodegradable polyphosphates with various topologies (such as, linear, star and hyperbranched ones) were facilely synthesized via successtive SCROP of different cyclic phosphates. They were promising candidates for drug carriers (Scheme 12).[440-446]

Thin film of hyperbranched glycoacrylate, poly(3-*O*-acryloyl-α,β-D-glucopyranoside) (HPAGlc), was immobilized on PTFE-like fluorocarbon surface via low pressure plasma. The results of protein adsorption, cell adhesion and proliferation measurements indicated HPAGlc could control biointerfacial phenomena.[447]

6.5 Dispersion and surface modification by HPs

Because of the highly branching structure, less intermolecular entanglements are involved in HPs, which endow them with good solubility, low viscosity and special rheological property. Their unique 3D architecture offers the large enough steric hindrance avoiding aggregation of nanoparticles. Therefore, HPs are good dispersions and surface modifiers of nanoparticle.[448]

Due to the remarkable mechanical, thermal, and electrical properties, carbon nanotubes (CNTs) can be used as the extra reinforcing additives to strengthen polymer matrices. However, keeping CNTs full and stable dispersion in polymer matrix is a big challenge, owing to the great surface property defference between CNT and matrix. Direct grafting of HPs on CNT can effectively solve this issue. Here, HPs act as the dispersant for CNT and compatilizer for the matrix.[449-458]

Growth of HPs onto CNTs will generate HP brushes or molecular nanoforests to improve dispersing stability of CNTs. In this regard, a series of works on CNTs-based polymer brushes by *in situ* SCVP, SCROP, polycondensation or layer-by-layer self-assembly technique were reported.[449-453] Fig. 24 showed the synthesis of hyperbranched poly[3-ethyl-3-(hydroxymethyl)-oxetane]-grafted multiwalled carbon nanotubes (MWCNTs) and corresponding TEM images of the product.[449] The polymer layer was about 12.5 nm covered on the MWNT.

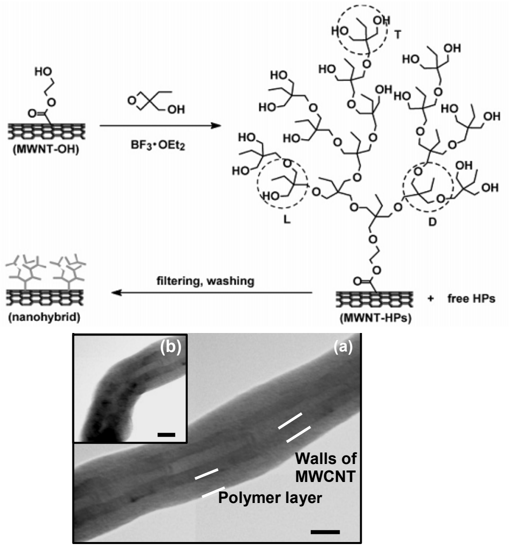


Fig. 24 Synthetic route of HPG-*g*-MWCNTs and corresponding TEM images. The insert (b) shows the TEM image of the bent area of functionalized CNT. The scale bar is 20 nm. (Reproduced from ref. 449 with permission of the American Chemical Society).

Hyperbranched poly(phenylene sulfide) grafted MWNTs (HPPS-*g*-MWNTs) were prepared via two-step Friedel-Crafts acylation reaction.[454] Both the dispersability and processability of HPPS-*g*-MWNTs were enhanced significantly by the grafting of HPPSs.

Incorporation of hydrophilic polymer grafted CNTs into the hydrophobic membrane can improve its surface hydrophilicity and protein resistance.[455-457] Hyperbranched poly(amine-ester) modified MWNTs (HPAE-*g*-MWNTs) were employed to prepare HPAE-*g*-MWNT/PVDF nanohybrid membranes.[457] Hydrophilic HPAE-*g*-MWNT covered on the surface of PVDF reducing water contact angle and protein adsorption. The flux recovery ratio of PVDF membranes increased from 82% to 95.7%, implying the antifouling capability was significant enhancement.

6.6 HP-based nanocomposites/hybrids

Nanocomposites/hybrids exhibited better performances than those of any components because of their favorable synergetic effects.[459,460] HPs possess the low intrinsic viscosity, endowing nanocomposite/hybrids with good processability. Nanoparticles can introduce some specific functions (such as flame retardancy, *etc*.) into nanocomposites/hybrids and improve their mechanical and thermal properties.[459]

There are two main methods to prepare nanocomposites or hybrids: i) direct mixing HPs with inorganic nanoparticles, and ii) *in situ* polymerization in the presence of nanoparticles.[460] If HPs and nanoparticles were linked by covalent bonds, the phase interface can be efficiently eliminated and overall performances will be largely enhanced.

6.6.1 HP-based nanosilica hybrids

Growth of HPs on nanosilica surface will generate stable HP-nanosilica hybrids. Firstly, spherical silica nanoparticles were modified by 2-bromo-isobutyryl bromide to afford the initiator. Secondly, the initiator was used to synthesize HP-silica hybrids via *in situ* SCVP.[461-465]

The epoxy functionalized alkoxysilane was added into the mixture of epoxy resin and phenolic group-ended HPs.[466] After the curing of epoxy groups by UV irradiation and the sol-gel reaction of alkoxysilane, HP toughened scratch resistant hybrid coatings were obtained.

Via the amidation of amino groups, ethoxysilyl moiety was introduced into polyamic acid and 3-(triethoxysilyl) propyl succinic anhydride (TESSA).[467] By the sol-gel reaction with tetraethoxysilane (TEOS) and following imidation, polyimide-silica hybrid films (with 40 and 50 wt % of silica) were prepared. The resulted polyimide-silica films exhibited the permselectivity for CO_2/CH_4 separation. [468]

6.6.2 HP-POSS nanohybrids

Chlorine- or bromine-containing polyhedral oligomeric silsesquioxane (POSS) nanoparticles can react with the hydroxyl of HPI, affording the POSS modified HPI nanohybrids. The hybrid layers possess low dielectric constants (up to 2.54).[469]

POSS-containing hyperbranched polyethylenes (HPEs) were synthesized via chain walking copolymerization of ethylene and acryloisobutyl-POSS.[470] POSS moieties reduce significantly the intrinsic viscosity and improve the thermal oxidative stability of the products.

6.6.3 HP-clay nanocomposites

Clay, such as montmorillonite, with natural lamellar structure has been widely used in organic-inorganic nanocomposites. Except the improvement of strength, flame retardation, thermotolerance, *etc.*, introducing layered nanoparticles into matrix can greatly enhance the barrier property of matrix which mainly depends on the content and dispersion of layered montmorillonite. The formed tortuous pathways efficiently retard the progress of diffusion molecules. Moreover, as HPs take part in the crosslinking reaction, their abundant functional groups can generate the more compact networks which also benefit the barrier performance.[471-474]

6.6.4 HP-graphene oxide hybrids

In recent years, graphene has attracted increasing attention and gained a rapid development because of its unique atom-thick 2D structure[475], excellent performances and wide range of promising applications.[476] Compared to graphene, graphene oxide (GO) possesses plentiful available groups (hydroxyl and epoxide groups) at their sheet edges,[477] which facilitate further chemical modifications. Furthermore, these functional groups endow GO sheets with strong hydrophilicity, which makes GO fully disperse in water or polar solvents (such as DMF).[478] All these merits allow GO to be a good cadidate for nanocomposites.

Generally, HPs exhibit very poor strength, owing to their weak entanglements. Therefore, HPs are rarely used as materials individually. Gao *et al.* employed HPG as binders and added into GO suspensions to develop nacre-mimic continuous fiber via wet-spinning assembly strategy. With “brick-and-mortar” lamellar structures of alternating GO sheets and HPG binders, HPG-GO fibers exhibited excellent mechanical properties, high electrical conductivity and remarkable corrosion resistance.[479]

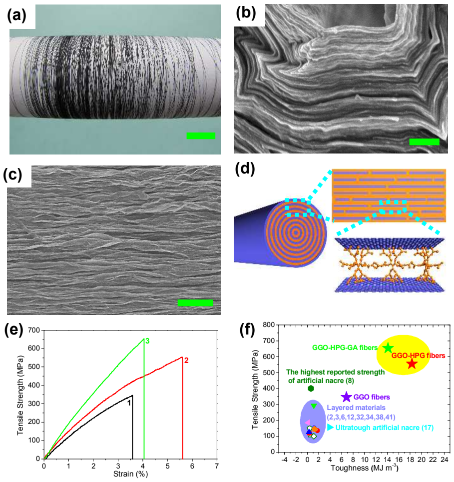


Fig. 25 Photograph of 30 m long GO-HPG gel fibre (a, scale bar of 10 mm). SEM images of cross-section of a GO-HPG gel fibre (b and c, scale bars of 250 nm and 3.0 μm, respectively); wet-spinning assembly of complex LCs into nacre-mimetic fibres with hierarchical structures (d); typical stress-strain curves for neat GO (1), GO-HPG (2), and GO-HPG-GA (3) fibres (e); the strain rate is 10% per minute (f). (Reproduced from ref. 480 with permission from Nature Publishing Group).

Through liquid crystal self-templating methodology, the next generation of continuous nacre-mimics with ultrastrong and tough properties were achieved.[480,481] Hierarchically assembled fibers exhibited the highest tensile strength (652 MPa), 5 to 8 folds as high as that of nacre (80-135 MPa), and excellent ductility with toughness of 18 MJ m^{-3}, 10 to 20 times greater than that of nacre (0.1-1.8 MJ m^{-3}). These outstanding mechanical performances of GO-HPG fibers are ascribed to its hierarchically assembled structure and the uniform alignment of GO sheets (Fig. 25).

Apart from the self-assembly induced by hydrogen bonding interactions, another reliable approach is grafting of HPs onto GO nanosheets. Hyperbranched polysiloxane (HPS) functionalized GOs were prepared via the *in situ* condensation of trimethoxyl silicane and hydroxyl groups of GOs.[482] The resulted HPS-*g*-GOs reacted with dicyclopentadiene bisphenol dicyanate ester resin to produce the novel PU composites. Compared with the control PU, the impact and flexural strengths of HPS-*g*-GOs modified PUs were enhanced by 60% and 47%, respectively.

The *N*-isopropylacrylamide (NIPAM) partially modified HPEI (HPEI-PNIPAM) was synthesized via Michael addition, followed by the epoxy-amide addition between imino groups from HPEI and epoxy groups from GO. PNIPAM moieties presented the thermosensitivity, indicating that the nanocomposite can be used for biomedical or biosensor fields.[483-486]

6.7 HP-based coatings

HPs possess highly branched structures, rendering especially lower viscosity and good flow properties. Besides, their irregular molecular structures can reduce the likelihood of crystallization, making them be high transparence. Consequently, HPs are suitable coating resins. So far, they have been widely used as UV-curable, waterborne, and powder coatings, *etc*.

6.7.1 UV-curable coatings

Compared with those thermally activated systems, UV-curable coatings can be crosslinked at lower temperature and almost have no emission of volatile organic compounds. For heat-sensitive substrates (such as plastic and wood), UV-curable coatings will not cause substrate deformation which is a big challenge to heat curing one.

Unsaturated double bond-terminated HPs are main components in UV-curable coatings. With diverse backbones, HPs have been designed and synthesized for UV-curable flame retarded, hydrophobic, powder and waterborne coatings.[487-489]

The hyperbranched polyphosphate acrylates (HPPAs) were synthesized via Michael addition of tri(acryloyloxyethyl) phosphate (TAEP) and piperazine and exploited for UV-cured coating. The highest tensile strength (31.7 MPa) and elongation at break (2 folds that of cured TAEP) were obtained as the feed ratio of HPPA and TAEP was 2:8. With the increasing content of HPPA (from 0 to 20 wt %), the limiting oxygen index (LOI) values decreased from 47.0 to 34.0, illustrating the TAEP has the dominant effect to the flame retardancy.[487] By similar synthetic protocols, hyperbranched polyphosphonate acrylate (HBPPA)[474] and melamine-based hyperbranched polyphosphonate acrylate (MHPA)[475] were facilely synthesized. Both of them exhibited good flam retardancy and UV-curing property.

6.7.2 Protective coatings

One of major functions of protective coating is to prevent metal substrates from corrosion or scratch. The protection performance and service life depend on its crosslinked density.

Hyperbranched poly (ester-urethane-urea) (HPEUU) was used to make anticorrosive coating using hydroxyl-ended HPEs (OH-HPEs) and isophorone di-isocyanate (IPDI) as starting materials. Compared with linear counterparts, their mechanical, durability and corrosion resistance properties were improved significantly, due to higher crosslinked density. [490]

Moisture cured isocyanate-terminated HPUs were prepared via the addition of isocyanante (NCO) and hydroxyl group (OH) of HPG.[491] The ratio of NCO/OH and the molecular weight of HPG have a crucial effect on mechanical and thermal properties of the cured coating. Tensile strength, hydrophobility and char residue value enhanced with the increasing of the NCO/OH ratio.

6.7.3 Antifouling coatings

Conventional antifouling approaches are through releasing toxic metal ions or biocides to inhibit proliferation of organisms. This strategy may bring about some undesired side effects. Such as, the released toxins are harmful for environment. Because of the electrostatic repulsion and interfacial hydration effects, PEG can inhibit protein and cell adsorption. Introducing PEG moieties into coatings can endow them with good biofouling prevention property.[492-495]

HPEI was firstly coupled to a polydopamine-coated stainless steel substrate. Using HPEI as a platform, various modifications were carried out via the thiol-epoxy coupling, thiol-ene and thiol-Michael addition.[496] The resultant stainless steel-P(HEMA-*b*-SBMA) and stainless steel-PPEGMA surfaces can prevent bacterial adhesion.

QACs have been used as the bactericide in a contact-killing manner.[435] PVDF-*g*-PDMAEMA copolymers were synthesized, followed by quaternization of propargyl bromide and click reaction of N_3-HPG, to develop a microporous membrane with inhibiting bacterial growth and proliferation functions.[497]

6.7.4 Vegetable oil-based coatings

Vegetable oils (such as castor, soybean and palm oil, et al.) are the renewable, ecologically safe and biodegradable materials, which can be achieved from plant seeds. They are the general starting materials widely used in conventional coatings. Via careful molecular design, vegetable oils or their derivatives can be introduced into HPs, which may present unique performance for end applications.[498-500]

Two types of castor oil-based HPUs, MHPU and CHPU, were prepared using castor oil/monoglyceride, 1,4-butane diol, PCL and TDI as reactants.[498] MHPUs exhibited higher tensile strength, scratch hardness and gloss as well as lower elongation at break than those of CHPUs. Both of them showed good thermal and dielectric properties.

N,*N*'-bis(2-hydroxy ethyl) castor oil fatty amide, maleic anhydride, phthalic anhydride and isophthalic were reacted with diethanol amine to synthesize castor oil-based hyperbranched poly(ester amide)s (HPEAs).[499] HPEA was employed to crosslink epoxy resin for thermosetting coatings. It presented desirable properties including adhesion strength, scratch hardness, impact strength and so on, making it to be used as surface coatings. Additionally, the crosslinked coating was biodegradable due to the incorporating of renewable and degradable castor oil moiety.

6.8 HP-based modifiers

6.8.1 Toughenings or reinforcings

The diglycidyl ether of bisphenol A (DGEBA) resins are very useful precursors of thermoset materials. The rigid aromatic ring involved in their molecular chain leading to intrinsic brittleness, which has limited their applications. With the large free volume, epoxy-functional HPs have been exploited as modifiers to develop the toughness of cured DGEBA resin. [501,502]

The curable HERSS with DB of 0.71-0.84 was employed to prepare HERSS/DGEBA composites which exhibited better mechanical properties in comparison with those of pure DGEBA epoxy resins.[487] The improvements of tensile, flexural and impact strength were 76.4-88.6%, 25.3-36.0% and 78.4-92.1%, which were attributed to the formed ‘‘sea-island’’ structure (3.62-4.75 mm in diameter) in composites.

Reactive hyperbranched polyether (HPEE) was composed of the aromatic skeleton and terminal epoxy groups.[502] The modified DGEBA epoxy resin with 5 wt % HPEE showed a higher T_g than that of control sample. Although there was no phase separation involved in, properties of cured HPEE/DGEBA were improved significantly because of the high reactivity, rigid backbone and large mole free volume of HPEE.

Poly(styrene)-*b*-poly(ε-caprolactone) (PSOH-*b*-PCL) with an average DP_n of PCL arms of 60 has been prepared by the combining of ATRP and ROP.[100] PSOH-*b*-PCL could toughen cured epoxy resins by incorporating the linear PCL arms.

Except epoxy-functional HPs, hyperbranched polyimides,[503,504] poly(amidoamine),[505,506] poly(ester-amide),[507,508] and polyesters[509-514] were good tougheners or reinforcers for the cured DGEBA-based thermoset.

6.8.2 Thickening agents

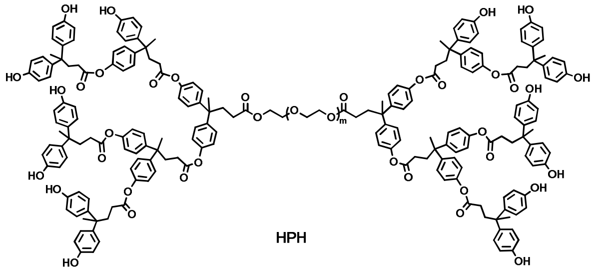
Star-like hyperbranched waterborne polyurethanes (HWPU) were composed of the hyperbranched core and hydrophilic linear arms.[515] The number of arms has an effect on the thickening effect of HWPU. Among them, the thickening effect of the HWPU with six arms was superior to that of the ones with four and twelve arms. Furthermore, with the same core, the thickening effect was relevant to the length of hydrophilic chain and the hydrophobic terminal group content.

Hyperbranched poly(DVB-*co*-PDMS) was synthesized via deactivation enhanced atom transfer polymerization (DE-ATRP) of PDMS and divinylbenzene (DVB). It was further applied as thickening agent for silicon oils. Within the coating, cosmetic and pharmaceutical fields, the viscosity-modifier showed a well-controlled effect.[516]

6.8.3 Curing accelerants

With the hyperbranched-linear-hyperbranched structure, the copolymer, HPH, was prepared by condensation of 4,4-bis(4-hydroxyphenyl) valeric acid and poly(ethylene glycol) in one-pot (Scheme 13).[101] Because of abundant peripheral phenolic hydroxyls, addition of HPH in the mixture of epoxy and hardener could accelerate the crosslinking of 3,4-epoxycyclohexylmethyl-

3',4'-epoxycyclohexyl carboxylate epoxy resin, as declared by thermal- and photo-DSC detections.



Scheme 13 Schematic illustration for HPH.

6.8.4 Hydrophobic modifiers

Fluoroalkyl- or silane-containing HPs have been utilized as surface modifiers to regulate the surface tension of polymer matrices, affording the hydrophobic surface.[517]

Two classes of fluorocarbon-containing HPs (HPEFs/HPUFs) exhibited very low surface free energies (13.67-24.49 mJ m^{-2}).[518] The resulted low surface tensions mainly relied on the terminal short fluorinated chains. The cotton fabrics treated by HPEFs or HPUFs presented high hydrophobicity. Static contact angles were up to water of 146 °, hexadecane of 122 ° and decane of 102 °, respectively.

6.8.5 Low dielectric modifiers

Fluoro-terminated hyperbranched poly(phenylene oxide)s (FHPPOs) with DBs of 0.53-0.63 were synthesized by self-condensation.[158] The T_g of the product reached 164 °C as M_n was > 6, 800 g mol^{-1}. Low polarity of framework, plentiful fluorine-containing terminal groups and large free volume endowed FHPPOs with good dielectric property. Incorporation of FHPPO into DGEBA/2-ethyl-4-methylimidazole thermost could largely reduce the dielectric constant and water absorption. These results implied FHPPO was an effective *low-k* dielectric modifier.

6.9 HP-based membranes

Till now, HPs have been widely used as diverse membranes, such as nanofiltration membranes for water softening or water treatment[519-523], proton exchange membranes for fuel cells[524-526], gas separation membranes for chemical engineering[527-530] and antifouling/antibacterial membranes for bioapplications[531-533], *etc.*

Using 4-dimethylaminopyridine (DMAP) as the catalyst, trimesoyl chloride (TMC) and hyperbranched polyesteramide (HPEA) took place in interfacial polymerization to generate reverse osmosis membrane.[521] This composite membrane (thickness of ~100 nm) exhibited a high salt rejection. Such as, Na_2SO_4 rejection was up to 98% and NaCl and $MgSO_4$ rejections were > 92% with the water fluxes of around about 30-40 L·m^{-2} h^{-1} and the pressure of 0.6 MPa. Interestingly, the composite membrane could be used to separate organic compounds, such as PEG200.

Sulfonated star-hyperbranched polyimide (SHPI) membranes were synthesized for proton-transport.[525] As the electrochemical impedance spectroscopy (EIC) showed that the SHPI membrane exhibited high proton conductivity. At 80 °C and 98% RH, proton-transport rate reached 0.51 S cm^{-1} which was obviously superior to that of commercial Nafion®. Besides, the proton conductivity of the amphiphilic SHPI membranes was connected with the content of sulfonated-HPI moiety, because the channels of proton-transport were formed by the self-assembly of SHPIs.

Hybrid membrane composed of HPI/OH-HPI and silica was used for the CO_2/CH_4 separation.[530] Incorporation of silica into HPI/OH-HPI matrix enhanced significantly the gas permeability, which was ascribed to the larger free volume in the membrane and the synergistic effect of HPI/OH-HPI and silica.

Introducing hydrophilic polymer into hydrophobic membranes can greatly improve their antifouling property.[531] Addition of HPE-*g*-mPEG into poly(vinylidene fluoride) (PVDF) membranes by direct mixing, porous membranes were achieved by the phase inversion process. The water soluble mPEG modified porous membranes exhibited the low water contact angle (49 °), good antifouling and water flux recovery property.

In addition, HP-based membranes have been widely utilized in unit operations of chemical engineering,[534] such as distillation,[535] extraction,[536] absorption,[537] and so on. Details about these applications can be found in the recent review.[533]

6.10 Chemosensors

Conjugated polymer is a promising candidate for chemosensor to detect nitroaromatic explosives such as, picric acid (PA), 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT), *etc.*, because of its superior response and sensitivity to analytes.[538-547] However, intrinsic self-aggregation caused by polymer chains and induction of nitroaromatics will lead to emission quenching and decay of sensitivity.

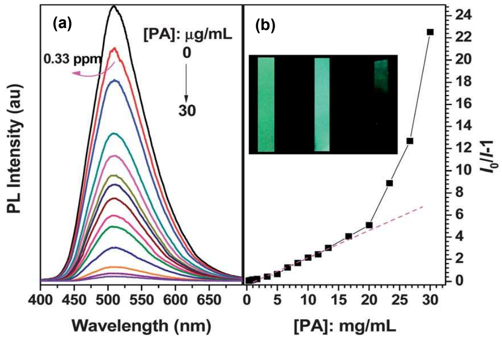


Fig. 26 Photoluminescence spectra of HP-TPE-Cz in THF–water mixture (1 : 9 v/v, 2.0 × 10^3 mg mL^{-1}) with different contents of PA (a); PA concentration dependance of intensity of HP-TPE-Cz in THF-water mixture, where I is peak intensity and I_0 is peak intensity at [PA] = 0 mg mL^{-1}(b); inset of (b): fluorescence images of HP-TPE-Cz specimens adsorbed in filter papers before (left), after being partially dipped into toluene (middle) and after being partially dipped into a toluene solution of PA (right). (Reproduced from ref. 545 with permission from Royal Society of Chemistry)

HCPs have the intriguing features, in comparision of their linear analogues: (i) high branching structures, endowing HCPs with desired AEE activity and signal amplification effect;[548-551] (ii) few entanglements among polymer chains, cutting the chance of the aforementioned autoaggregation largely;[1-3] (iii) numerous intramolecular cavities, affording high binding capability to analytes.[550-552] and (iv) 3D architecture, making excitonic migration and interaction between HCP and analyte easier;[553,554] In particularly, hyperbranched poly(silole)s,[538-540] polytriazoles,[541,542] poly(tetraphenylethene),[543,544] carbazole-containing HPs[545] and porous HCP nanoparticles[546,547] have been used as chemosensors for detection of nitroaromatics with superior sensitivity. For instance, tetraphenylethylene-based HCP (HP-TPE-Cz) quenching could be clearly discerned at a PA concentration as low as 0.33 ppm with the quenching constant of 3.99×10^4 M^{-1}, due to its higher AIEE activity and signal amplified effect (Fig. 26).[545]

6.11 Other applications

6.11.1 Shape memory materials

Shape memory polymers (SMPs) are those materials can keep deformation in a temporary state and can recover their primal shapes as they are subjected to the specific external stimuli. This deformation and recovery process corresponds to the reversible storage and release of entropy energy.

PCL-based HPUs,[555] HPU-MWCNTs[556] and HPU-GO[557] have been served as advanced thermo-responsive SMPs.

6.11.2 Self-healing materials

Self-healing materials can spontaneously heal injuries as the organism does. This advanced function of artificial polymer is attributed to the formed physical or chemical network. Imposing damage on it leads to partial nocovalent bonds fracture. On the contrary, the injury healing process corresponds to the reconstruction of the broken nocovalent or covalent bonds. Consequently, the dynamic physical/chemical networks play a crucial role in the self-healing materials.

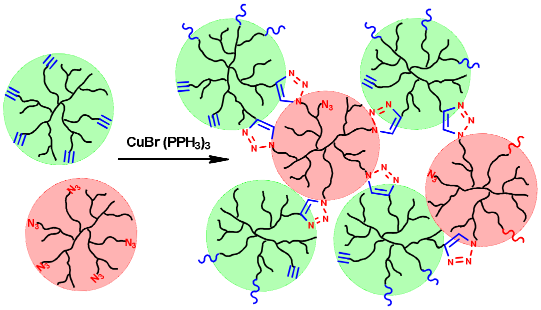


Fig. 27 Crosslinking hyperbranched azide- and alkyne-functionalized PIBs by CuACC reaction at 20 °C.[558]

Azide- and alkyne-ended hyperbranched poly(isobutylene)s (HPIBs, M_n = 25,200-35,400 g mol^{-1}, with ~9 terminal groups) were employed to synthesize self-healing HPs via the CuAAC.[558] Because of high molecular mobility of HPIB chains (T_gs of -60 to -70 °C), the product showed a self-healing behavior (Fig. 27).

6.11.3 Elastomers

Generally, elastomers have low T_g, ultrahigh molecular weights, and a suitable degree of crosslinking. Low T_g endows the elastomer with a large deformability and the modest degree of crosslinking makes its deformation to be restorable.

PU has been widely used as elastomers. Introducing hydroxyl-functional HPs into PU elastomers, the products have better mechanical properties than those of linear counterparts.[559-561]

6.11.4 Adhesives

Adhesives serve as the important media to link up two or more objects. The good wettability, strong interfacial interaction and high mechanical performances are essential features of an adhesive.

Hyperbranched poly(triazole)s were used as the adhesives and showed the high adhesive strength at ambient temperature (such as 16.49 ± 1.21 MPa) and at 200 °C (7 times of epoxy adhesive 4006# and GY-1#) due to their abundant rigid aromatic and triazole rings. Moreover, the strong polar triazole groups give rise to large binding energy between the HP-based adhesive and metal substrates.[183]

Besides, HPG-based PUs and hyperbranched poly(dopamine-*co*-acrylate)s have been used as non-toxic adhesives, possessing the promising application in biological fields.[562, 563]

6.11.5 Printing inks

Similar to paints, aside of good rheological property, the high quality printing ink should have high adhesive force, bright color and good color fastness.

Two classes of hydroxyl-ended HPEs, Boltorn™ P500 and P1000, were firstly applied to modify commercially available printing ink Urania®.[564] Both of the modified flexographic printing inks by Boltorn™ P500 or P1000 showed better coloring fastness, compared to the control sample.

6.11.6 Catalysts

Related contents of HP-stabilized transition metal complexes/ catalysts have been illustrated in **6.2.2**. Here, we introduce HPs directly used as catalysts.

Hyperbranched polyselenides can act as catalyst due to a lot of diselenide groups on the skeleton.[565] Diselenide groups showed a glutathione peroxidase like catalytic property. Moreover, cobalt-containing poly [tris(4-ethynylphenyl)-amine] (HPTEPA) has been used as the efficient catalyst for the preparation of CNTs by CVD approach.[566]

6.11.7 CO_2 capture materials

Amino groups can react with CO_2 forming the carbamate which chemical property is unstable. The carbamate is easily decomposed at elevated temperature. Based on the mechanism, amino-containing HPs can be applied to CO_2 capture materials.

To improve CO_2 adsorption capability, amino-functionalized HPs are usually coated on the surface of mesoporous silica skeleton to enlarge the effective contact area between CO_2 and amino groups.[567-569] Amino-containing HPs have exhibited higher CO_2 capture capacity and desorption efficiency than amino-containing silane couplings modified mesoporous silica skeleton.

6.11.8 Microporous materials

Hyperbranched poly(phenylene butadiynylene)s and poly(phenylene ethynylene)s with the rigid skeletons were prepared via Hay-Sonogashira coupling reaction.[570] As the TGA measurement revealed, their thermal degradation process displayed two stages. The first stage (300-500 °C) was ascribed to the elimination of side chains and afforded microporous polymers (surface areas of about 800 m^2 g^{-1}). The second stage (> 900 °C) was attributed to the degradation of backbones. Correspondingly, the microporous carbon was formed (surface areas of ca.13 m^2 g^{-1}).

6.11.9 Battery materials

HPG was used to prepare the gel electrolyte for dye-sensitized solar cells (DSSCs).[571] Increasing of the HPG content can enhance the open circuit voltage of DSSCs and improve the energy conversion efficiency (up to 6.78% at 1 sun).

Sulfur-rich HPs (SRHPs) were synthesized via the thiol-ene like addition of elemental sulfur and 1,3-diidopropenylbenzene in chloroform.[572] Then they were utilized as the cathode materials in Li-S cells. Due to avoiding the possibility of elemental sulfur involved in cathode material, the Li-S cell exhibited good battery properties, such as high initial capacities (1247.6 mA h g^{-1}) and good cycle performance (167.2 mA h g^{-1} after 400 times) which outdistanced that of pure sulfur (Fig. 28).

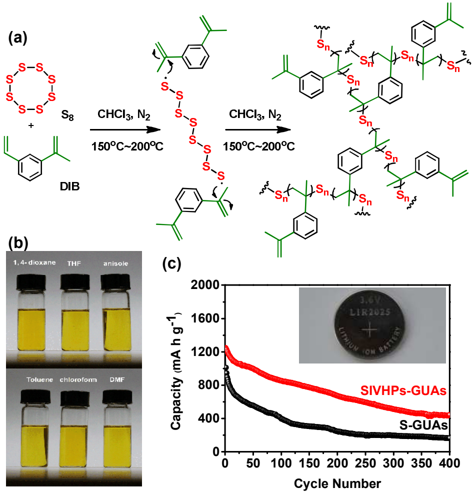


Fig. 28 Sulfur-rich HPs (SRHPs) used for battery materials. Structure of SRHP (a), the good solubility of SRHPs in different organic solvents (b), and cycle performance of Li-S cells using SRHPs as the cathode materials (c). Insert shows the Li-S cell fabricated using SRHPs as the cathode material in figure 28c. (Reproduced from ref. 572, with permission from the Royal Society of Chemistry).

6.11.10 Supercapacitors

Vinyl-terminated hyperbranched poly(siloxysilane)s (VHPSis) were synthesized via the hydrosilylation.[573] VHPSis were filled in the gap between aluminum oxide and poly-(3,4-ethylenedioxythiophene) (PEDOT) to develop interfacial properties. The formed VHPSi layer could reduce the degradation of oxide film and lower the conductivity of PEDOT electrode. Consequently, the VHPSi-modified aluminum solid electrolytic capacitor showed a high capacitance (410 μF) and a low equivalent series resistance (5.6 mΩ).

7. Conclusion and outlook

This review has summerized the major developments of structure control, synthetic strategies, functionalizations as well as applications of CHPs and SHPs since 2004. Various robust click chemistries, including CuAAC, MFAAC, SPC, thiol-ene/yne addition, Menschutkin quaternization reaction, Diels-Alder cycloaddition, Michael addition, *etc.*, have been employed for the synthesis of HPs based on the SMM, DMM, CMM and MCM in an orthogonal manner. The HPs can be further functionalized from its periphery to core through these efficient click chemistries, affording tailored structures and properties. Notably, for functionalization of the core of HPs, it largely depends on their structures. With the loose framework and the lower steric hindrance, all the scaffolds of SHPs were functionalized. On the contrary, the backbone functionalization of CHPs only reached around 70%, owing to their highly compact structures. HPs with the highly branching structures, abundant functional groups and unique properties have shown great potential applications for light-emitting materials, biomaterials, supramolecular chemistry, nanoscience and technology, hybrid materials and composites, coatings, adhesives, and so on.

Although the large advances have been achieved in the past decades, several major challenges still exist.

Firstly, how to precisely control DB, chemical structures, M_ws and PDIs of HPs? All the parameters are very important for their performances and further applications. With regard to linear polymers or dendrimers, their corresponding polymerizations can be well controlled. However, for HPs, the effective control of these parameters is very difficult, since the chain propagation is intricate and elusive.

Secondly, how to facilely introduce hetero-atoms (such as N, P, S, Se, *etc.*) and/or hetero-functional groups into HPs? Such hetero-atoms/-functional groups-containing HPs have exhibited fascinating and unique performances. For instance, nitrogen- and phosphorus-containing HPs are flame retardency; sulphur-containing HPs possess refractive index; and selenium-containing HPs are the promising candidate for biomaterials. However, more effective methods are required to easily introduce these designed hetero-atoms into HPs.

Thirdly, how to successfully synthesize plane (2D) HPs? Although soluble linear (1D) and spherical (3D) macromolecules have been well developed, so far, no plane HPs had been reported. The synthesis and applications of 2D HPs may become a new research hotspot in the near future.

Fourthly, how to facilely develop sequence-controlled HPs? Just recently, the first hetero-functional sequence-controlled HP has been synthesized via the thiol-yne polymerization.[172] With the unqiue architecture, the novel HPs will attract more interests and become the scientific mainstream.

Fifthly, how to effectively apply these artificial HPs in the service of humanity? Linear polymers had a broad range of uses since it first appeared, whereas the hyperbranched analogue has few practical applications till now. Combining the relationship between structure and property and making a new breakthrough in synthetic methodology for HPs further promote the development of this subject.

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Notes and references

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