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Progress in synthesis, modification, characterization and applications of hyperbranched polyphosphate polyesters

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ABSTRACT

Hyperbranched polyphosphate polyesters (HPPs) as a special class of hyperbranched polymers have attracted increased interest and have been intensively studied, because of peculiar structures, excellent biocompatibility, flexibility in physicochemical properties, biodegradability, water soluble, thermal stability, and mechanical properties. HPPs can be divided into phosphates as monomers and phosphates as end groups. In this article, the classification, general synthesis, modifications, and applications of HPP are reviewed. In addition, recent developments in the application of HPP are described, such as modified or functionalized by end capping and hypergrafting to improve the performances in polymer blends, coatings, flame retardant, leather. Furthermore, the modifications and application of HPPs in biomedical materials, such as drug delivery and bone regeneration were discussed. In summary, the hyperbranched polymer enlarges its application range and improves its application performance compared with conventional polymer. In the future, more new HPPs composite materials will be developed through hyperbranched technique. This review of HPPs will provide useful theoretical basis and technical support for the development of new hyperbranched polymer material.

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Hyperbranched polyphosphate polyester; synthesis; modification; application

1. Introduction

Hyperbranched polymers are highly branched macromolecules with three-dimensional dendritic structure, and they are prepared through a one-step polymerization process. They have been intensively studied during the past last 20 years due to their unusual properties, such as low viscosity, high solubility and good compatibility with other materials. As for dendritic polymers, core-based, randomly hyperbranched polymers are potentially attractive and the architectural features are responsible for the extensive proposed applications of these advanced materials [1,2]. In general, hyperbranched polymers are divided into four parts including hyperbranched polyphenyls [3], hyperbranched polyethers [4–6], hyperbranched polyamides [7–9] and hyperbranched polyesters [10–12]. Structurally, hyperbranched polyesters have a large number of degradable ester bonds in the main chain and have good biodegradability. Hyperbranched polyphosphate has degradable phosphoric acid diester bonds in its main chain, and since the structure of this polyphosphate is similar to that of nucleic acid, it has good biocompatibility and biodegradability. Widely used in medical field, paint, flame retardant and other fields. Hyperbranched polyphenylene has good solubility, a large number of terminal modifiable groups and low viscosity coefficient, which are used in the field of functional materials, chemical sensors, metal nanoparticles preparation.

Hyperbranched polyphosphate polyesters (HPPs) as part of HBPEs also play important roles because of their specific structures. Unlike other HBPEs, HPPs contain a hyperbranched architecture, namely HPPs will possess the comprehensive advantages of polyphosphate esters and hyperbranched polymers [13]. It is known that the HBPEs have the unique structures and properties. As for the polyphosphates, they have received great attention in the past few years owing to their good biocompatibility, biodegradability, and the structural similarity to nucleic and teichoic acids [14]. Meanwhile, we know that the chemistry of polyphosphate esters is at the origin of a wealth of potential applications in materials science (e.g. biology, drug release systems, pharmacology, in the buildup of fire retardant coatings, mineral and material processing, detergent industry as dispersants and rheological modifiers, food science and technology) [15]. Thus, many researchers integrated the advantages of

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the two kinds of polymers to study a novel polymer. Recent years, the potential applications of hyperbranched polyphosphate esters have used in many fields of drug delivery [16], biomedical materials [17], flame retardants [18], coatings [19], foaming agents [20], and epoxy resin [21]. In addition, the potentials of HPPs are growing rapidly according to the increasing number of publications.

A number of papers concentrated on hyperbranched polymers, covering hyperbranched polyphenyls, hyperbranched polyethers and hyperbranched polyesters of their synthesis, modifications, and applications [22]. However, as far as we know, no comprehensive reviews on synthesis, modifications, and applications of HPPs have been reported up to now. Therefore, it is necessary to explore the synthesis, modifications, and applications of HPPs.

2. Classification, synthesis and characterization of HPPs

2.1 With phosphates as monomers to synthesize HPPs

The synthetic techniques used to prepare HPPs can be divided into two categories [23]: (1) polycondensation of AB_2 monomers; (2) polymerization of two types of monomers or a monomer pair, such as A_2+ B_3 monomers, A_3+ BB´ monomers, and A_2+ $BB´_2$ monomers. Among them, the AB_2 and A_2+ B_3 polymerizations are the main approaches.

2.1.1 HPPs based on AB_2 monomers

A large number of HPPs reported in the literature are prepared from stepwise growth polycondensation of AB_2 monomers. The AB_2 monomers, 2-(2-hydroxyethoxy) ethoxy-2-oxo-1,3,2-dioxaphospholane (HEEP), have most frequently been used as starting materials to prepare HPPs. This method is characterised by the fact that when the A and B groups selectively react with each other, a branched polymer without cross-linking is produced. It is also possible to obtain polymers with low polydispersities, and high degrees of branching.

The HEEP is a typical AB_2 inimer with a reactive five-membered cyclic phosphate and a primary alcoholic hydroxyl as the initiating moiety. During polymerization, the alcoholic hydroxyl in one HEEP molecule initiates the ring-opening reaction of the five-membered cyclic phosphate in another HEEP molecule to afford a dimer with one five-membered cyclic phosphate and two primary alcoholic hydroxyls. Further, the ring-opening reactions of HEEP and dimer may result in two kinds of trimers. Finally, the hyperbranched polyphosphates (HPHEEPs) have been synthesized, and the high molecular weight HPHEEPs are produced by subsequent addition reaction and condensation of the formed various species. With the different reaction time and temperature of the polymerization of HEEP, the solubility of HPHEEPs is different. With the increase of polymerization time, the molecular weight and molecular weight distribution increase, and the solubility varies with the polymer structure. For example, the HPHEEPs, which was obtained form 120 h at 60°C, were soluble in water, methanol, and ethanol, and partly soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF) due to its large number of phosphate and terminal hydroxyl groups, but insoluble in tetrahydrofuran (THF), dichloromethane and chloroform etc. However, when the polymerization was performed for 10.5 h at 90°C, the HPHEEP became insoluble in water and alcohol solvents. As the polymerization time prolongs, the molecular weight gradually increases and reaches its maximum value within a certain period of time. The solubility deteriorates with the increase of molecular weight [24]. This may be attributed to some side reactions occurring at higher reaction temperature that led to the gelation of the reaction system. The molecular weight of the products as well as the width of the molecular weight distribution by gel permeation chromatography (GPC) increased with the polymerization time. These data maybe indicate that the reversible transesterification and depolymerization macromolecules occurred and reached the dynamic balance during the polymerization due to the pentavalent nature of phosphorus [25,26]. However, the molecular weight measurement via GPC was based on the hydrodynamic volume of polymers, and the hydrodynamic volume of hyperbranched polymers was smaller than the linear polymer with the same M_W. Accordingly, the authentic was higher than the obtained due to the limitation of the GPC test in the hyperbranched polymers [27,28]. The degree of branching (DB) is the most important molecular structure parameter for hyperbranched polymers and is determined by the techniques of ^{1}H NMR, quantitative ^{13}C NMR and ^{31}P NMR spectra [29,30]. We can find the dendritic units, terminal units and linear units through ^{1}H NMR and ^{13}C NMR spectra, and the signals of phosphorus atoms can be identified in the ^{31}P NMR spectrum. From the above analysis, we can determine the DB of HPPs.

Liu et al. [31] synthesized hyperbranched polyphosphates with terminal hydroxyls through self-condensing ring-opening polymerization (SCROP) of HEEP. Figure 1 shows the synthesis route of the AB_2 monomer and HPHEEP-OH via a SCROP approach. The AB_2 was synthesized by a five-membered cyclic phosphate and a primary alcoholic hydroxyl. It is well-known that

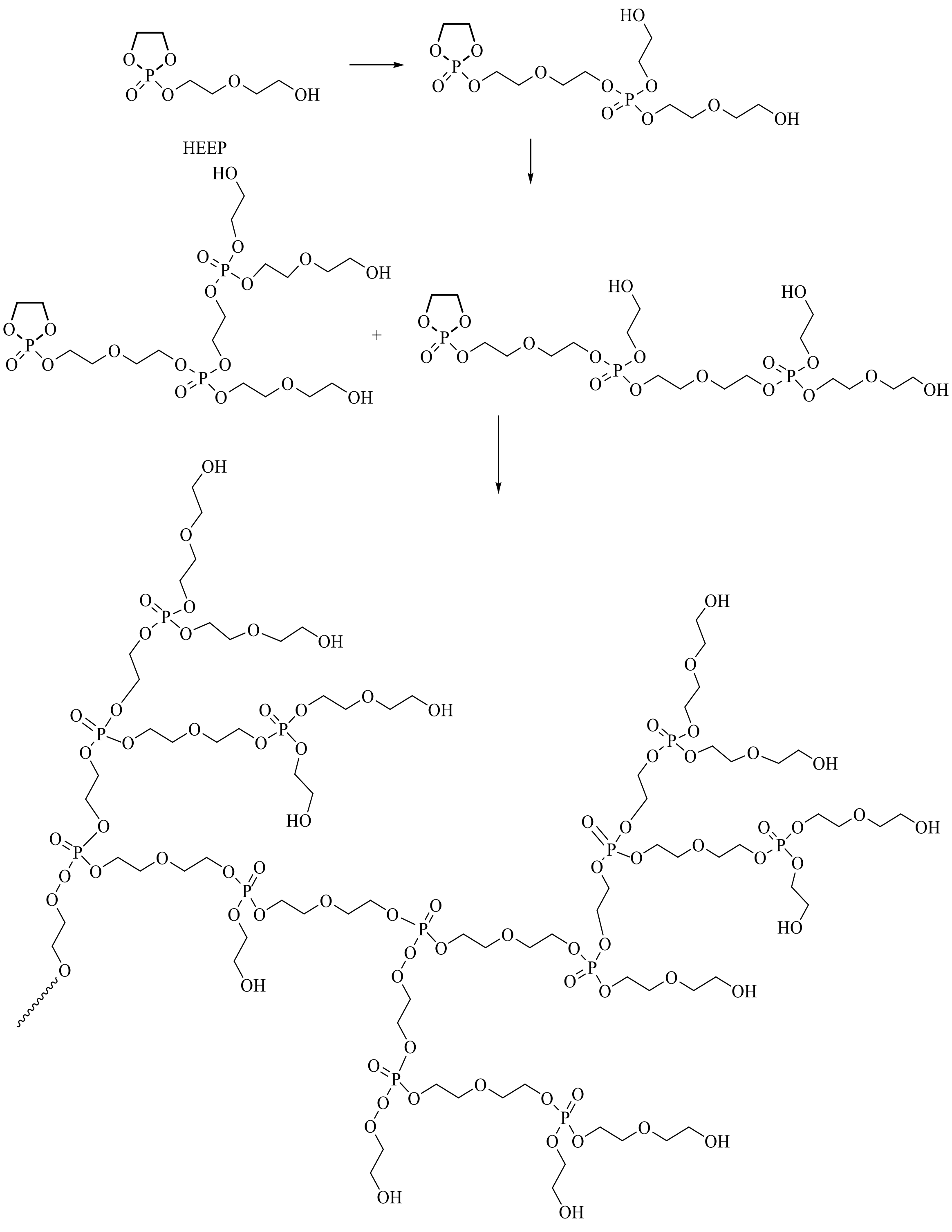


Figure 1. Schematic description for the synthesis of the AB_2 monomer and the HPHEEP-OH. [31] Copyright 2009, Macromolecules. [41] Copyright 2006, Polym Degrad Stabil. [51] Copyright 2009, Prog Org Coat. [52] Copyright 2014, Polym Degrad Stabil. [63] Copyright 2022, Polym Chem. [70] Copyright 2010, Langmuir. [76] Copyright 2022, ECS Trans. [79] Copyright 2010, Biomaterials. [107] Copyright 2020, Polym Degrad Stabil. [108] Copyright 2021, Cellulose. [114] Copyright 2012, Polym Degrad Stabil. [118] Copyright 2021, Prog Org Coat. [125] Copyright 2022, Bioconjugate Chem. [75] Copyright 2011, Chem Eng & Technol. [133] Copyright 2023, Polym Chem..

primary alcoholic hydroxyls can initiate the ring-opening polymerization of five-membered cyclic phosphates. Therefore, it is easy to react with the alcoholic hydroxyl in diethylene glycol (DEG) because of the high reactivity of chlorine atom in 2-chloro-2-oxo-1,3,2-dioxaphospholane (COP). All the samples of (HPHEEP) were synthesized by the bulk polymerization of HEEP at different temperatures without a catalyst. Meanwhile, they investigated the conversion dependence of structural units and DB of the HBPE by ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectroscopies.

2-[(2-Hydroxyethyl) disulfanyl] ethoxy-2-oxo-1,3,2-dioxaphospholane (HSEP) was another monomers, which was synthesized by COP and 2-hydroxyethyl disulfide, and triethylamine (TEA) as catalyst. Then, the hydrophobic hyperbranched polyphosphate of HPHSEP-OH with disulfide bonds in the highly branched backbone was prepared through SCROP of HSEP monomer with a 2-((2-hydroxyethyl) disulfanyl)ethyl pendant group [32]. Molecular weight and polydispersity index were 1.12×10^4 g/mol and 1.72 by GPC.

Furthermore, a number of terminal hydroxyl groups in this biocompatible and biodegradable hyperbranched polyphosphates will provide a unique opportunity for further modification and functionalization. HPPs would be modified according to our requirements.

2.1.2 HPPs based on A_2+ B_3 monomers

With the methods of the $A_2 + B_3$ as the monomers to synthesis the HPPs has been reported, which is the most commonly mature method. The synthetic method is simple, without separation and purification step by step, and polymer structure can keep their original characteristics and properties, so this is the most important mean for the synthesis of hyperbranched polymers. The disadvantage is that the molecular weight of the polymer is difficult to control, and the molecular weight distribution of the product is relatively wide. The synthetic methods of HPPs by $A_2 + B_3$ approaches are solution polycondensation and melt polycondensation generally. It is well known that direct polycondensation of A_2 and B_3 monomers generally results in gelation [33–35]. Thus, there are many methods to overcome this crucial problem to obtain soluble three-dimensional macromolecules, such as stopping the polymerization through precipitation or endcapping prior to the critical point of gelation, by the slow addition of monomer, or by using special catalysts and condensation agents. We can synthesize different branched algebra through adjusting the mole ratio of monomer. As we all know, the monomer feed ratio, monomer addition manner, and concentration strongly influence the polymerization. Hyperbranched products are only obtained under highly restricted reaction conditions [36,37], so it is necessary to choose the suitable reaction conditions avoiding gelation. The A_2+ B_3 approach allows the composition of the two monomers to be altered and thus opens pathways to tailor the properties, if one knows how the monomer sequence and the DB will be affected upon changing reaction conditions. We often use the approach to avoid gelation for preparing hyperbranched polymers from A_2 and B_3 monomers is to conduct solution polymerization wherein a dilute solution of one monomer is slowly added to a dilute solution of another monomer. Furthermore, the order of addition of the monomer solution will significantly influence the structures of the final products [38]. When the A_2 dilute solution is slowly added to the B_3 dilute solution, maybe the gelation can be avoided and hyperbranched polymer is obtained. In contrast, when the B_3 dilute solution is added to the A_2 dilute solution, it generally results in gelation. We can prevent crosslinking through control of a certain molar ratio of di-to trifunctional monomers [39].

Huang et al. [40] synthesized a halogen-free phosphorus-nitrogen containing hyperbranched polyphosphate acrylate (HPPA) and a phosphorus-containing monomer, tri(acryloyloxyethyl) phosphate (TAEP). They used anhydrous piperazine as A_2 monomer and TAEP as B_3 monomer to synthesize HPPA-0.8, HPPA, and HPPA-1.2, in mole ratios of 1:0.8, 1:1 and 1:1.2, respectively. According to the research, the mode of the addition of monomer also had effect on the molecular weight, and the number-average molecular weights (M_ns) of the HPPAs were almost around 30000–60000 g/mol by GPC. Meanwhile, HPPA presented low viscosity at room temperature with its high molecular weight, and the viscosity of samples went down sharply when adding co-monomer TAEP into HPPA due to the destruction of inter/intramolecular chain entanglements resulting from the lower viscosity of TAEP. As for glass transition temperature (T_g), there was a decrease in the T_g from 105°C to 50°C with increasing HPPA content. Such a decrease can be ascribed to the lower crosslinking density and a greater level of flexibility and mobility of the molecular chain of HPPA.

Wang et al. [41] synthesized hyperbranched polyphosphate ester (HPPE) used as a reactive-type flame retardant by employing an A_2+ B_3 polycondensation. The HPPE as A_2 (bisphenol-A) (BPA) and B_3 (phosphoryl trichloride) ($POCl_3$) monomers in the absence of gelation were determined. A_2 and B_3 monomers were dissolved in N-methylpyrrolidinone (NMP) at low levels, while pyridine was used as a catalyst. In the case of NMP and pyridine, the reaction conditions, such as the initial molar ratio of A_2 and B_3 monomers. ^{31}P NMR measurement reveals that dendritic units only appear and increase at high conversion. Figure 2 shows the synthesis route of the HPPE via a polycondensation approach. For the properties of T_g, the higher temperature as HPPE

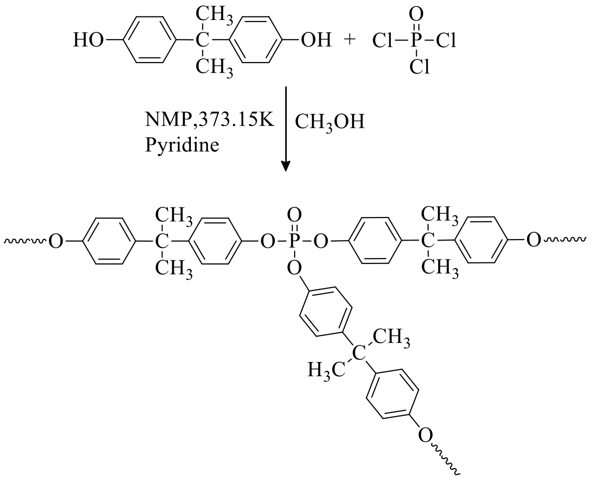


Figure 2. Schematic description for the synthesis of the HPPE [41].

content increased, the higher crosslinking density it produced. The T_g values of the HPPs were 156°C, 159°C, 164°C of 1 Hz, 5 Hz, 10 Hz, respectively.

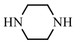
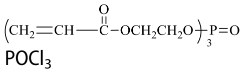
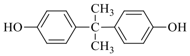
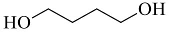
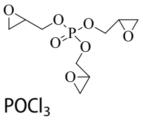
Some A_2 and B_3 monomers used for preparation of HPPs and the mode of polymerization are summarized in Table 1. Chlorine atoms in phosphorus oxychloride are very easy to react with the alcoholic hydroxyl in the 1,3,5-tris(2-hydroxyethyl)cyanuric acid because of high reactivity of the phosphorus oxychloride, so B_3 monomer usually is the phosphorus oxychloride ($POCl_3$).

Epoxy-terminated hyperbranched polyphosphate (E-HBPP) by employing an A_2+ B_3 polycondensation via proton transfer polymerization was synthesized. E-HBPP was mixed with diglycidyl ether of bisphenol-A (DGEBA) in different ratios to obtain a series of flame-retardant epoxy resins. The Bu_4NCl was chosen to be the catalyst because the chloride-ion catalysis was proved effective for controlling the polymerization to avoid crosslinking. The mechanistic basis lied on the equilibrium between the epoxide ring opening by chloride ion and the base-induced ring closure of the resulting chlorohydrins [44]. The number average molecular weight and polydispersity index were 5100 g mol^{-1} and 1.69, respectively. Thermal property of the HPPs was an important factor for their application from TG curve. According to the chemical structure, the segments of the HPPs are made up of three kinds of bonds, including C-N, C-C and P-O according to its chemical structure. The C-N bond is much easier to break than C-C bond because of its lower bonding energy. For the thermal degradation behaviors, it was investigated by thermogravimetric analysis and in situ FT-IR and showed that the phosphate group of E-HBPP first degraded to form poly(phosphoric acid) s at around 300°C, which had a major contribution to form the compact char to protect the sample from further degradation for applications. The final char yield increased from 2.2% to 13.1% with HPPE.

Some researchers have synthesized the HPPs containing other elements, such as diselenide-polymers. Because the synthesis of diselenide-containing polymers involve in remarkable ability, but a low solubility and poor stability [45,46], so adding the hyperbranched polymer with a number of diselenide bonds inside may improve the solubility and better stability. The hyperbranched polyselenide (HPSe) was synthesized via the polymerization of the diselenide-containing diol as A_2 monomer with phosphorus oxychloride as B_3 monomer under an alkalescent environment. The resulting HPSe has a highly branched structure with alternative diselenide and phosphate groups in its backbone framework. The weight-average molecular weight of HPSe characterized by GPC is 6100 g/mol with the polydispersity index of 1.7.

As for the properties of HPPs, the reactive monomers, and sometime, organic solvents, are generally added into to adjust the formulation's properties, such as viscosity, solubility and mechanical properties. Most of HPPs present low inherent viscosity, this may be due to their large numbers of low-polar end-groups of HPPs, which inhibited the formation of inter/intramolecular hydrogen bonds. The glass transition temperature (T_g) is a very important parameter for materials because it establishes the service environment for the materials' usage and it varies widely with the structures, molecular weights and other thermodynamic parameters of the polymers, such as intermolecular force and chain flexibility [47]. The effect of crosslinking density to T_g is greater than that of chain flexibility, leading to a higher

Table 1. A_2 and B_3 monomers used for preparation of HPPs and the mode of polymerization.

A_2 monomers	B_3 monomers	Polymerization mode	Reference and year
	 $\left(CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}OCH_2CH_2O\right)_3P{=}O$	Solution	[40] 2007
	$POCl_3$	Solution	[41] 2006
		Melt	[42] 2007
HO-R-SeSe-R-OH	$POCl_3$	Melt	[43] 2012

T_g with HPPs, and the T_g is not greatly affected by the set frequency during testing.

2.1.3 HPPs based on A_2+ BB'_2 monomers

The approach for preparing hyperbranched polymers from a BB'_2 type monomer and an A_2 type monomer has been developed [48–50]. In the BB'_2 monomer there is one B functional group and two B′ functional groups that have different reactivities with A group due to different chemical environment. In Flory's gelation theory, if the B groups have different reactivities, soluble hyperbranched polymers with high molar mass can be obtained.

Wang et al. [51] synthesized of a phosphorus-nitrogen containing hyperbranched polyphosphonate acrylate (HBPPA) used as a flame-retardant oligomer in UV-coatings by employing an A_2+ BB'_2 type polycondensation. The di(acryloyloxyethyl) benzenephosphonate (DABP) was used as an A_2 component and N-(2-aminoethyl)-piperazine was used as a BB'_2 component. The schematic outline of synthesis route for DABP as A_2 monomer and HBPPA is given in Figure 3. The number average molecular weight (M_n) of HBPPA was measured experimentally to be 4200 g/ mol by GPC. As the reaction proceeds, the higher crosslinking level eventually limited the mobility of monomers and oligomers as well as the radicals, which meant the propagation reaction was controlled by the diffusion of fragments in the system.

2.1.4 HPPs based on A_3+ BB′ monomers

The approach of A_3+ BB′ as monomers is not commonly used. As for this approach, the B′ has a higher reactivity than B, and it is anticipated that cross-linking will not occur if an asymmetric monomer BB′ is used. The basic principle of A_3+ BB′ is shown in Figure 4.

Li et al. [52] prepared hyperbranched poly(phosphamide ester) oligomer (HBPE) via A_3+ BB′ method. It was synthesized by $POCl_3$ as the A_3 monomer and $H_2NCH_2CH_2OH$ as the BB′ monomer, and the schematic outline of synthesis route for HBPE is given in Figure 5. The number average molecular weight was 1000 g/mol and weight molecular weight was 1300 g/mol with the molecular distribution of 1.3. It was obviously that the authentic value was higher than the obtained due to the limitation of the GPC test in the hyperbranched polymers.

2.1.5 HPPs based on A_3+ B_3 monomers

At present, there are few applications of the method of A_3+ B_3 monomers [53], due to the two monomers can be shaped into branched structure, so we can imagine the molecular structure of the polymer will be closer, meanwhile, they show different characteristics than A_2+ B_3. About the A_3+ B_3, the A and B have the same activity, respectively. The average numbers of functional groups of the monomers are easily to from gels, therefore it is suitable for the preparation of the gels [54]. The monomer feed ratio is the direct method for preventing gelation, and reaction conditions such as temperature, concentration and catalysts strongly influenced the reaction.

Chen et al. [55] synthesized the hyperbranched polyphosphate ester (HPPE) based on the 1,3,5-tris(2-hydroxyethyl)cyanuric acid (THEIC) as the A_3 monomer and the $POCl_3$, with a K_2CO_3 catalyst. The definition of the DB,

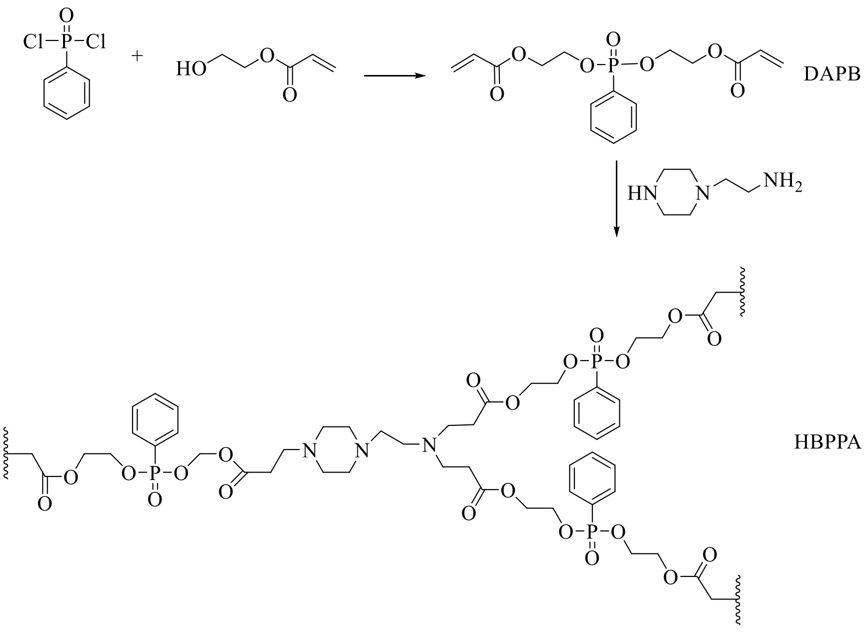


Figure 3. Schematic illustration for the synthesis of DABP and HBPPA [51].

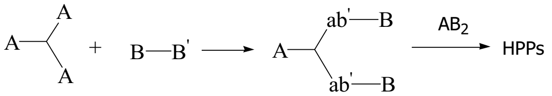


Figure 4. A_3+ BB´ approach to HPPs as a typical example for the basic principle description.

according to the polymerization mechanism of the HPPE [56,57], the DB can be calculated by Equation (1), which N_b means branching unit, N_t means terminal unit and

$$DB = (N_b + N_t)/(N_b + N_t + N_L) \quad (1)$$

N_L means linear unit.

Through the ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra analysis, the DB of HPPE-1, HPPE-2 and HPPE-3 obtained were 0.90, 0.91 and 0.87, respectively. The molecular weights of the HPPE-1, HPPE-2 and HPPE-3 by MALDI-TOF-MS measurement were 1530, 1768 and 2750 g/mol, respectively. Thermal property of the HPPE was an important factor for application, and thermal degradation of the HPPE-2 should have two stages from a TG curvy. In the first stage, the thermal degradation temperature of the HPPE-2 weight loss ratio is 22.2 wt% and the weight loss ratio of 49.1 wt% in the second stage. The residual weight of 25 wt% is mainly from P_2O_5 resulted from the HPPE-2 degradation.

2.2 Without phosphate as monomer to synthesize HPPs

The HPPs could be synthesized on the basis of an amphiphilic hyperbranched multi-arm copolymer without phosphate as monomer, and with polyphosphate as arms. Polyphosphates are often called 'condensed phosphates' since they are polymers of phosphate anions and are obtained by repeated condensation of [PO_4] units [58]. The physicochemical properties and the molecular mass distribution of polyphosphates are mainly related to the average chain length [59]. There are many ways to control the topological structure of polymers, such as ring-opening polymerization (ROP) of cyclic monomers [60,61], SCROP of cyclic esters [62] and solution/melt polycondensation of phosphorus compounds. Hyperbranched polyesters with a large number of terminal hydroxyl groups are often used as the core of amphiphilic hyperbranched multi-arm copolymers, and grafted polyphosphates. For the polyphosphates, cyclic phosphate monomers (CPMs) is used by the reaction of COP and R commonly (R = ethyl; isopropyl; 2-hydroxyethyl). Because of the high reactivity of chlorine atom in COP, it is often used as the precursor to react with the alcoholic hydroxyl and produce CPMs with different pendant groups. Figure 6 is the synthetic routes of CPMs with different pendant groups. The design of hyperbranched polymer can benefit from their unique core-shell structure, and hyperbranched multi-arm copolymers have been prepared as unimolecular micelles to overcome the disadvantages of classical micelles [63,64]. Furthermore, the HPPs would possess good biocompatibility, biodegradability, and structural similarity to nucleic and teichoic acids [65,66]. Consequently, hydrophilic polyphosphates may be an

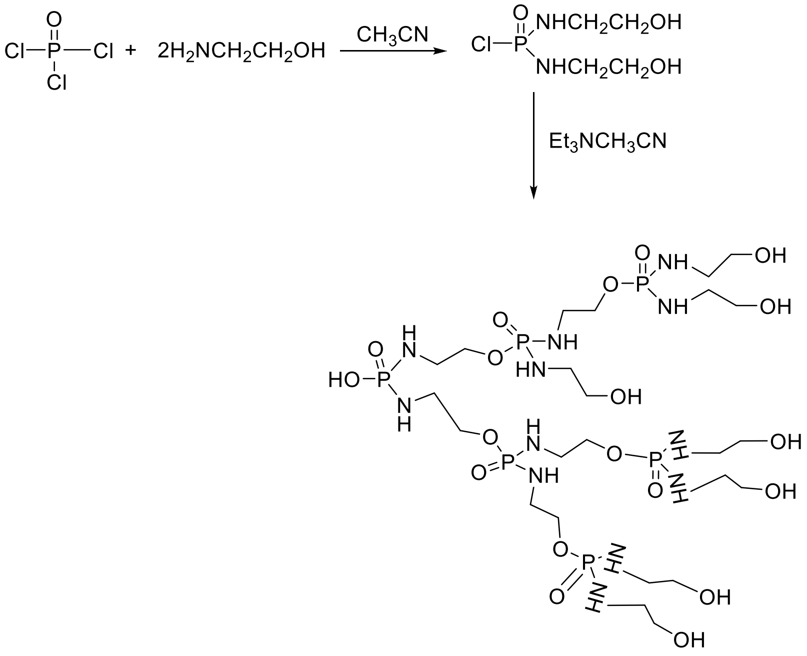


Figure 5. Schematic illustration for the synthesis of HBPE [52].

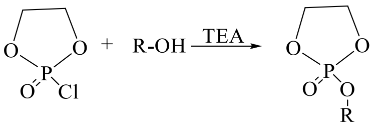


Figure 6. Synthetic routes of CPMs with different pendant groups [63].

interesting alternative to the reported hydrophilic segments as the outer shell of micelles [67–69]. Figure 7 is the schematic illustration of reaction route.

Liu et al. [70] reported a novel type of amphiphilic hyperbranched multi-arm copolymer [H40-*star*-(PLA-b-PEP-OH)] (Figure 8), which was synthesized through a two-step ROP procedure and applied to drug delivery. The schematic illustration of H40-*star*-(PLA-b-PEP-OH). The H40-*star*-(PLA-*b*-PEP-OH) based on the boltorn H40 (H40) core, the poly(L-lactide) (PLA) inner shell, the poly (ethyl ethylene phosphate) (PEP) outer shell, and the Sn (Oct)$_2$ as a catalyst was synthesized by the ROP of LA and EP. Firstly, H40 was used as macroinitiator for the ROP of L-lactide to form the intermediate (H40-*star*-PLA-OH). Then, the PEP was further initiated to produce H40-*star*-(PLA-b-PEP-OH). The architectures of PLA and PEP blocks can be easily controlled during the ROP processes, the stability and the properties could be improved by adjusting the hydrophobic/hydrophilic balance. The resulting hyperbranched multi-arm copolymers were characterized by ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR, GPC, and FTIR spectra. The molecular weights of H40, H40-*star*-PLA-OH, and H40-*star*-(PLA-b-PEP-OH) were 0.3×10^4 g/mol, 10.5×10^4 g/mol and 15.0×10^4 g/mol, respectively. In addition, the DB of PLA and PEP blocks could be easily controlled by adjusting the molar ratio of LA/EP to hydroxyl groups in the feed during the ROP processes.

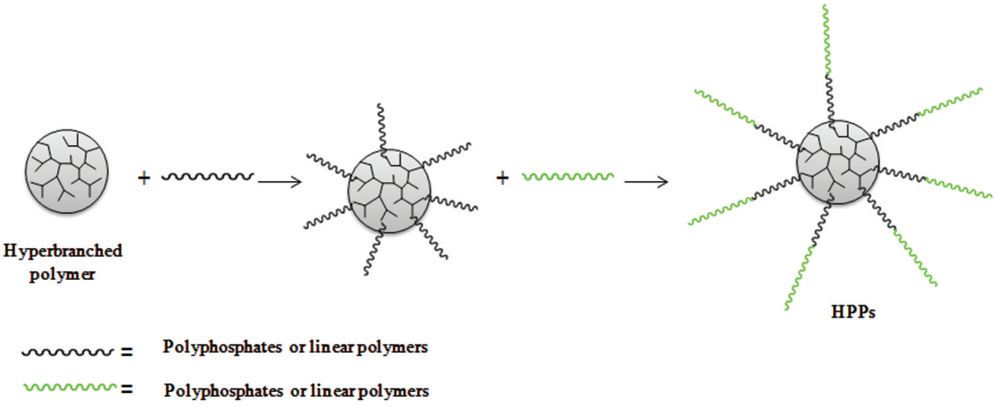


Figure 7. The schematic illustration of reaction route.

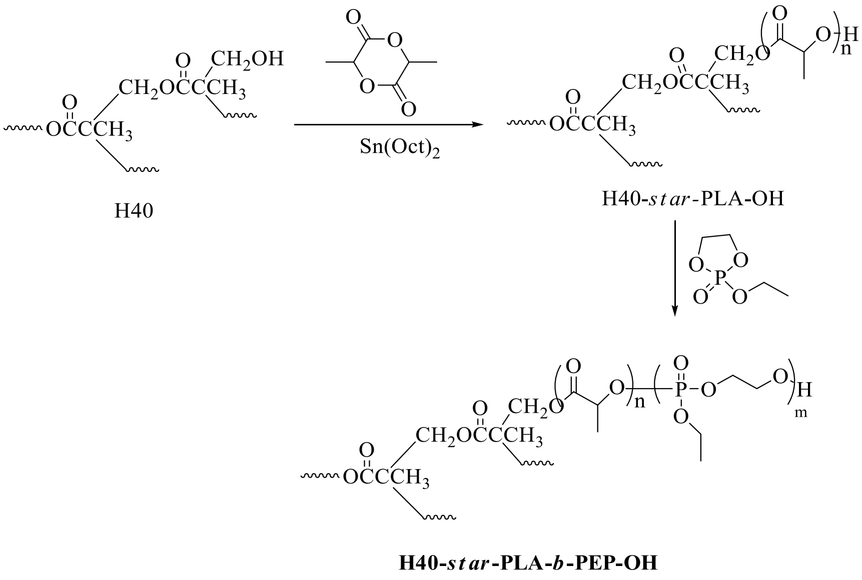
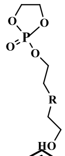
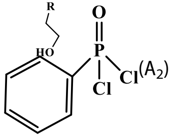
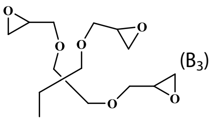
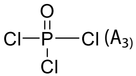
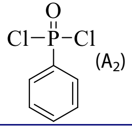
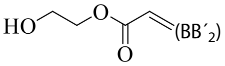


Figure 8. The schematic illustration of synthesis H40-*star*-(PLA-b-PEP-OH) [70].

Table 2. The application of these polymers.

Monomers	Monomers	Polymerization mode	Application	Reference and year
		self-condensing ring-opening polymerization	Biomedical	[71] 2013
		Melt	Flame Retardant	[72] 2010
 $Cl-\overset{O}{\underset{Cl}{P}}-Cl$ (A₃)	$H_2NCH_2CH_2OH$ (BB′)	Melt	UV cured film	[52]2012
		polycondensation	UV-coatings	[51] 2009

Due to the ease of polymerization without catalyst, the purity of the product special physical, chemical properties and good rheological properties, it will be an ideal material for biomedical, flame retardants, coatings and other fields. In addition, the large number of terminal hydroxyl groups in this biocompatible and biodegradable hyperbranched polyphosphate provides a unique opportunity for further modification and functionalization, as shown in Table 2.

2.3 Characterization of HPPs

As for structures of HPPs, there are some normal examination methods, such as ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, 2D NMR (^{1}H, ^{1}H-COSY and ^{13}C, ^{1}H-HSQC) spectra, FT-IR spectra, MALDI-MS-TOF spectrometer, 3D FT-IR/TG analysis and soon [73–75]. The main difficulty is that the linkage between P = O group and the three units (branching, linear and terminal units) is taken into account for analyzing the chemical structures of polyphosphate ester, so there are many kinds of different chemical structures (Figure 9), and the T means terminal unit, L means linear unit and B means branching unit. The structures of HPPs could be appeared in ^{31}P NMR spectra, respectively.

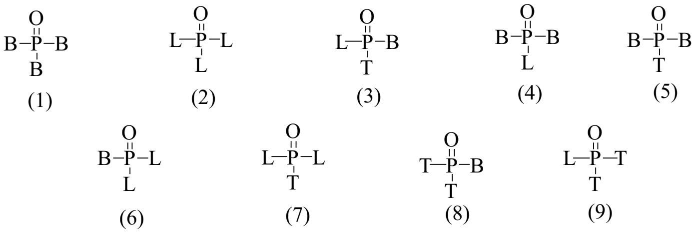


Figure 9. Chemical structures of the hyperbranched polyphosphate esters.

3. Modifications of HPPs

Hyperbranched polymers are often modified to satisfy their properties for specialized purpose and applications, meanwhile the type of end groups determines to a

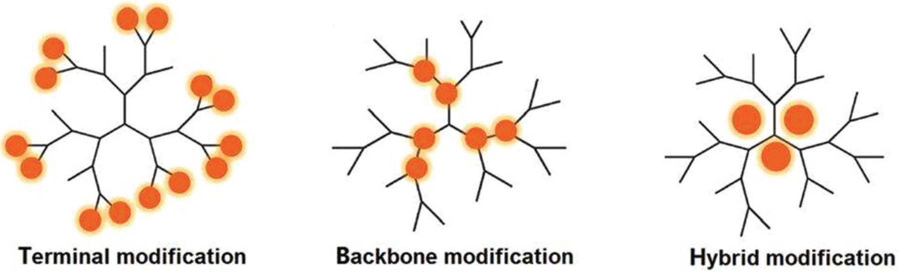


Figure 10. HBPs can be modified in three different ways: terminal modification, backbone modification and hybrid modification [76].

considerable extent the physical properties. The properties of hyperbranched polymers are strongly influenced by the functional chain end groups and the nature of the backbone (Figure 10) [76]. As for HPPs, three major modification methods have been developed: (1) terminal modification; (2) backbone modification; (3) hybrid modification.

3.1. Terminal modification

The large number of functional end groups attached to the terminal units of hyperbranched polymers can be conveniently end-capped with small organic molecules. In the end-capping process, the major purposes are emphasized to fabricate novel functional polymeric materials. Many experiments demonstrated that the polyphosphates have been concerned on development of the functional polymers. On the other hand, they also have investigated the effect of end groups on the properties.

HPHEEP-OH is a primary HPP to modify. Because of the large number of surface functional hydroxyl groups, it could be modified to enhance specific performances, such as biocompatibility, biodegradability, micelle stability, drug loading ability and light reversibly. Figure 11 is the schematic diagram of synthetic HPHEEP-OH.

Many experiments demonstrated that the terminal functional groups strongly influenced the micelle structures, CMC and size of a hyperbranched polymer. For the micelle structures, an amphiphilic polymer can form a core/shell structure in water. The inner core of micelles consists of the hydrophobic linear arms and the shell of micelles composed of the hydrophilic hyperbranched polymer [77,78].

Liu et al. [79] composed the hydrophilic core and hydrophobic multi-arm of HPHEEP-*star*-PPEPs by hyperbranched and linear polyphosphates respectively. The HPHEEP-OH was synthesized by SCROP of 2-(2-hydroxyethoxy)ethoxy-2-oxo-1,3,2-dioxaphospholane (HPPE). HPHEEP-*star*-PPEP-1, −2, and −3 were synthesized by ROP of 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane (PEP) used HPHEEP-OH and $Sn(Oct)_2$ as the macromolecular initiator and catalyst, respectively. The number average molecular weight of hyperbranched core HPHEEP-OH was about 3400 g/mol measured by GPC. By increasing the initial molar ratio PEP/hydroxyl, the number average molecular weights of HPHEEP-*star*-PPEPs increased clearly from 4800 to 10300 g mo^{-1}. In addition, HPHEEP-*star*-PPEPs can self-assembly into nanocarriers in aqueous media with controlled size from 48 to 74 nm by conveniently adjusting the length of hydrophobic arm. Clearly, the average diameter of the micelles increases with the molecular weight. The length of hydrophobic multi-arm can be controlled simply by adjusting the initial molar ratio of multi-arm/hydroxyl, so the molecular weight could be controlled by initial molar ratio (Figure 12).

The performances of HPPs would be extended through introducing the functional molecules, such as photochromic molecules, electrochromic molecules and electroluminescent molecules. Spiropyran (SP) is a well-investigated photochromic molecule which can undergo an isomerization between hydrophobic SP and hydrophilic merocyanine (MC) [80]. Chen et al. [81] synthesized an amphiphilic spiropyran-modified hyperbranched polyphosphate (HPHEEP-SP) by combining the reversible light-responsiveness of carboxyl-containing spiropyran (SP-COOH) and the HPHEEP-OH. The amphiphilicity and light-responsiveness of HPHEEP-SP, the polymer could self-assemble into micelles with the ability to respond to different lights. Absolutely, the molecular design rendered HPHEEP-SP amphiphilic, and the hyperbranched polymer could self-assemble into micelles or other self-assemblies in aqueous solution. The micelles had a number-average hydrodynamic diameter (D_h) of 186.3 nm and a polydispersity of 0.216 which suggested the micelles have a narrow distribution by TEM and DLS measurements. The light with different wavelengths of the micellar solution was effects on the solution self-assembly behaviours of the polymers. When the micelles were irradiated with UV light, some amphiphilic HPHEEP-SP molecules in the micelles became totally hydrophilic molecules. After visible light irradiation, those hydrophilic molecules transformed back into amphiphilic molecules.

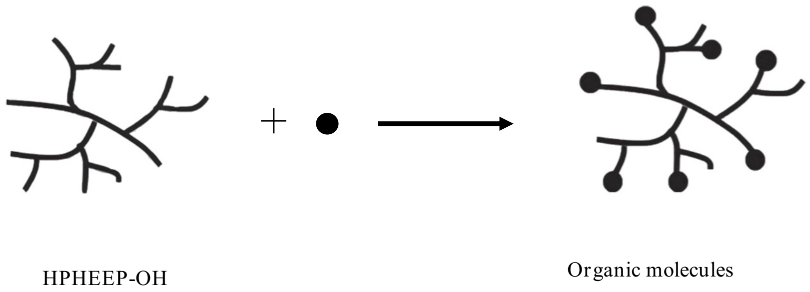


Figure 11. The schematic diagram of synthetic HPHEEP-OH by end-capping with organic molecules.

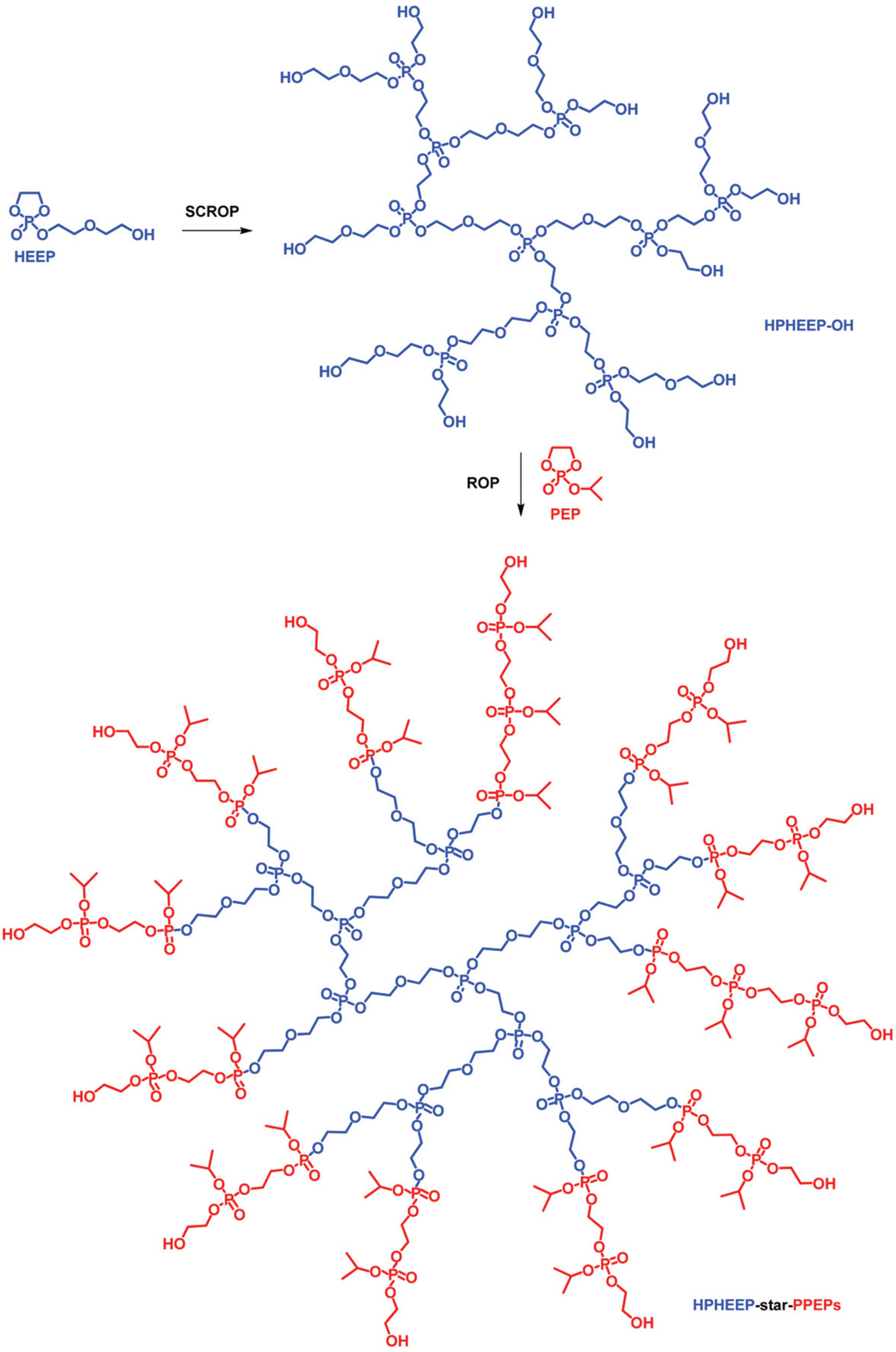


Figure 12. Synthesis route of HPHEEP-star-PPEPs [79].

3.2 Backbone modification

Another methods for modified of HPPs are hypergrafted with long chains, due to the combination of hyperbranched polymers and linear polymers or polymers, hyperbranched multi-arm copolymers possess a hyperbranched core and many long chains as arms. Hyperbranched polymers end-capping with long chains would have different kinds of properties by choosing different blocks. So, the performance of molecular would be investigated of their self-assembly behaviors, thermoresponsive behaviors and gene delivery and so on. As the same with the end-capping of organic molecules, most of HPPs is HPHEEP-OH. The long chains with the aliphatic alkyl and polymers have been reported recently.

For HPPs with the aliphatic alkyl, the phospholipid analogous amphiphilic polymers (HPHEEP-alkyl) have been synthesized by a polar hyperbranched polyphosphate headgroup and many hydrophobic aliphatic tails. Controlling the mole ratio of polar-hyperbranched polyphosphate and hydrophobic aliphatic could synthesized a series of modified HPPs through different proportions, such as CMC, diameter, PDI, T_g, T_m and even nanomicelle formation. Figure 13 is the schematic diagram of synthetic HPHEEP-OH.

Liu et al. [82] synthesized HPHEEP-alkyls by SCROP of 2-(2-hydroxyethoxy)ethoxy-2-oxo-1,3,2-dioxaphospholane and then capped with palmitoyl chloride. The $C_{16}H_{31}$ alkyl tails were attached by the reaction of terminal hydroxyl groups with palmitoyl chloride in DMF in the presence of TEA as an acid-binding to wipe off HCl. The numbers of consumed hydroxyl groups in HPHEEP-OH were 63%, 79% and 90% respectively and the corresponding specimens are named as HPHEEP-alkyl$_{0.63}$, HPHEEP-alkyl$_{0.79}$ and HPHEEP-alkyl$_{0.90}$. The structures and thermal properties of HPHEEP-alkyls were investigated by NMR, GPC, FT-IR, DSC and TGA. Grafting ratios of prepared HPHEEP-alkyls were 0.63, 0.79 and 0.90, respectively. The weight loss of HPHEEP-alkyls increases from 84.1% to 91.3% with increasing the alkyl molar content. The morphologies of nanomicelles showed that all HPHEEP-alkyls aggregated into approximate spherical nanomicelles or sigmoid shapes in water (Table 3).

As for the properties of HPPs-alkyls, the CMC is a key parameter describing the physical properties of micelles and relating to the thermodynamic stability of micelles [83]. So, the morphologies of nanomicelles are further studied by TEM measurement, and the CMC value and the concentration of amphiphilic could be determined by pyrene probe fluorescence spectrometry. Apparently, the average diameter of the aggregates increased with the numbers of alkyl tails. In other words, the more the alkyl tails, the larger the aggregates. In the selective solvent of water, the HPPs with long chains molecules maybe spontaneously self-assembled into nanomicelles driven by the strong hydrophobic/hydrophilic interaction of alkyl tails and hyperbranched polyphosphates [84]. As the concentration of HPPs-alkyls increases, the intensity ratio would increase and reach the characteristic level in completely hydrophobic environment at a certain concentration of HPPs-alkyls.

To investigate the thermal properties, the thermal stability of hyperbranched polyphosphates is improved when their terminal hydroxyls are capped by alkyls. When the alkyl tails are long enough, they can aggregate and crystallize to induce an intramolecular-phase separation and result in an increase of the T_g [85].

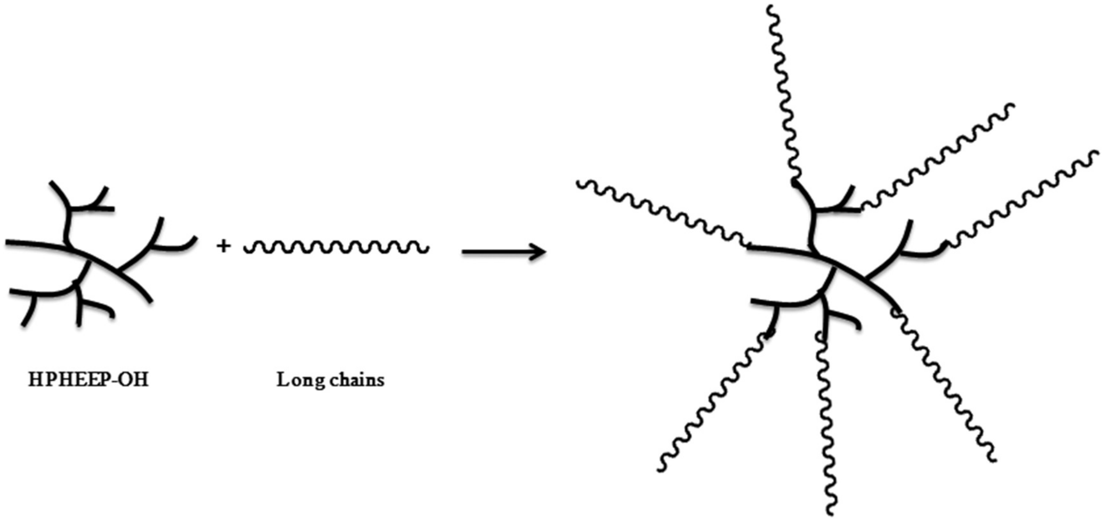


Figure 13. The schematic diagram of synthetic HPHEEP-OH by end-capping with long chains.

Table 3. Properties of polymers.

Sample	Mn	PDI	T_g (°C)	T_m (°C)	CMC (mg/mL)	Diameter (nm)
HPHEEP-OH	3240	2.98	−38.4	–	–	–
HPHEEP-alkyl$_{0.63}$	5500	3.13	−22.5	36.4	1.9×10^{-2}	98
HPHEEP-alkyl$_{0.79}$	6100	3.42	−14.0	37.6	1.1×10^{-2}	131
HPHEEP-alkyl$_{0.90}$	6500	3.73	2.0	38.5	3.9×10^{-3}	215

3.3 Hybrid modification

Hybrid modification is an effective method to synthesize organic/inorganic hyperbranched polymerization or to improve the surface properties of substances. Silicon surfaces can be grafted with hyperbranched polymers in large quantities, which is the main subject of research. Xia et al. [86] prepared a novel composite material grafted with dobby star hyperbranched block copolymers on the surface of SiO_2, using hydroxyethyl methacrylate and p-chloromethylstyrene as monomers by atom transfer radical polymerization. This modification method combines the respective advantages of organic and inorganic materials and expands the applications of hyperbranched polymers in the fields of catalysis, adsorption, and separation.

4 Applications of HPPs

HPPs have been considered for numerous applications because of the low viscosity of their solutions and melts, in many cases for their good biocompatibility, biodegradability, structural similarity to nucleic teichoic acids and good processability [87].

4.1 Blends with polymers

At present, polymer blends of homopolymers are necessary for applications. Polymer blends allow the optimization of some properties compared to that of isolated homopolymers, and hence they provide an economic way to create new materials with desired properties. The properties of the polymer blends are to a large extent determined by the morphology, i.e., the shape, size, and distribution of the components [88]. This makes it easily to blend with polymers to improve the properties. Blending HPPs with organic matters or linear polymers may be a route to synthesize novel materials. However, the interfacial properties between the two adjacent polymer phases are different and the least understood.

Many researchers have been devoted to study the incorporation of HPPs into polymers. As we all know, epoxy resins present the good electrical properties, good adhesion, low shrinkage, and resistance to heat, to mechanical shock, to solvents, and to chemicals [89,90]. Wang et al. [44] synthesized a novel HPPE and blended with bisphenol-A epoxy resin to improve its thermal stability and char yield. HPPE, BPA, and their blends in the ratios of 25/75, 50/50, 75/25 were used as curing agents. The cured specimens were denoted as $HPPE_0/BPA_{100}$, $HPPE_{25}/BPA_{75}$, $HPPE_{50}/BPA_{50}$, $HPPE_{75}/BPA_{25}$, and $HPPE_{100}/BPA_0$. When introduced HPPE, the T_g of the cured film of epoxy resin with HPPE (142.1°C) was found to be higher than that cured with BPA (133.4°C). This may resulted from the effect of crosslinking density, which could increase the T_g of the cured film [91]. So, when HPPs blended with epoxy resin, the T_g with higher temperature as HPPs content increases, the reason is that HPPs acts as a crosslinker, resulting in a much higher crosslinking density, and the effect of crosslinking density to T_g was greater than that of chain flexibility, leading to a higher T_g cured with HPPs. However, the combination between HPPs and diverse organic compounds, the regularities of T_g are different. It has been reported that the flexible -P-O- groups in the backbones of the cured polymers decrease the rotational barrier, so the T_g would decrease with incorporating phosphate-containing compounds [92]. In addition, the incorporated HPPs, which greatly reduce the rigidity of the polymer chains, cause chain motion at lower temperature. The hyperbranched polyphosphate acrylate/tri(acryloyloxyethyl) phosphate (HPPA) was mixed with di(hydroxylpropyl methacrylate) piperazine (DHMP) in different ratios, the dynamic mechanical thermal analysis results of the UV-cured films are listed in Table 4 [93]. The crosslink density increases from 2.869 for $HPPA_{50}/DHMP_{50}$ to 4.303 mmol cm^{-3} for pure DHMP. It is to be expected for the system with high unsaturation concentration, leading to more compact network. The T_g increases with increasing the DHMP content. The T_g may depend on the properties of organics or the reaction between HPPs and organics.

Table 4. T_g values (°C) of DMTA results of UV-cured HPPA/DHMP films.

Sample	T_g	v_2 (mmol cm^{-3})
HPPA50/DHMP50	69.8	2.869
HPPA40/DHMP60	72.4	3.244
HPPA30/DHMP70	80.4	3.518
HPPA20/DHMP80	89.8	3.859
HPPA10/DHMP90	94.8	4.207
DHMP	96.6	4.303

The mixture of the epoxy-terminated hyperbranched polyphosphate (E-HBPP) and bisphenol-A (DGEBA) of T_g was the same with HPPA/DHMP. The T_g and crosslink density increase when increasing the DGEBA content.

Except with oligomers, the HPPs can be blended with a variety of linear polymers, such as polycarbonate (PC), polyesters, polypropylenes, and polylactide (PLA). However, rarely study was found about the mixing method between HPPs and linear polymers. A hyperbranched polyphosphate bisphenol-A ester flame retardant (HPPEA) was prepared by using phosphorus oxychloride and bisphenol-A. HPPEA combined with melamine pyrophosphate (MPP) was incorporated into polyamide 6 (PA6) by Fang et al. [94].

Flame-retardant polylactide (PLA) composites were prepared using PLA and a hyperbranched polyphosphate ester (HPE) by Chen et al. [95]. The series of PLA/HPE composites containing 0 wt%, 5.0 wt%, 10.0 wt%, 15.0 wt% and 20.0 wt% content of HPE were prepared. The pyrolysis products from PLA20 released earlier than pure PLA because of the decomposition of HPE at low temperature. PLA containing a higher percentage of HPE exhibited relatively lower thermal stability at lower temperature while higher thermal stability at elevated temperature. The data of TG-IR showed that the presence of HPE catalyzed the degradation of PLA, and less combustible gas products were released at the thermal degradation process. The volatilized products were mainly aldehyde containing compounds, CO, aliphatic esters, and CO_2.

4.2 *Flame retardant*

The flame retardancy of polymers has always attracted much attention around the world because of the flammability of polymer materials. A typical phosphorus-containing flame retardant is generally made of three constituents: (1) an essentially phosphorus-containing additive; (2) another additive, containing nitrogen, such as melamine, urea, urea-formaldehyde resins and polyamides, which serves as a foaming agent; (3) carbon-containing additive, which acts as a carbon donor to allow an insulating cellular carbonaceous layer (char) to be formed between the polymer and flame [96]. There have been many methods to improve flame retardancy of flammable materials. Most of the flame retardants contain the nitrogen and phosphorus, but the toxic gases of N-flame retardant as hydrogen halides formed during combustion can choke people to death [97]. Therefore, much effort has been done to use phosphorus-based compounds as the substitutes of halogenated additives [98]. Recently, a promising way to improve fire resistance of flammable materials is to use intumescent flame retardants (IFR) which shows a lot of advantages such as high efficiency and production of low smoke and nontoxic gases [99,100]. Therefore, halogen-free compounds, especially phosphorus-containing compounds, were thought to be environment-friendly flame retardants because their combustion products are less toxic and corrosive, which made researchers devoted their energy to synthesize flame retardants using HPPs.

The most prominent use of HPPs is as flame retardants, because HPPs have some special advantages. As the polymeric flame retardants, owing to the high-molecular-weight, they show less toxic, low viscosity and low impacts on the physical properties of polymers. Meanwhile, the advantages between hyperbranched polymers and phosphate ester flame retardants were integrated, so it is a research direction of market value. Song and other researchers [101,102] have used the mixture of ammonium polyphosphate (APP) serving as acid agent and the other components as charring agent and blowing agent and were demonstrated that PLA/PEG/APP system had good charring ability and could improve the flame retardancy of PLA. Huang et al. [103] synthesized a series of hyperbranched polyphosphates to obtain UV-curable intumescent flame-retardant epoxy resins.

The performance of flame retardants could be commonly characterized by flammability, thermal degradation behaviour, char behaviour, and structure and morphology of carbonaceous residues. The thermogravimetric analysis (TGA) is the most commonly used technique for comparing and ranking the thermal stability of various polymers. As for HPPs, the lower thermal stability with higher phosphorus content at the beginning of thermal degradation is due to the lower stability of O = P-O bond compared with common C–C bond [104]. The second stage of weight loss with heat treatment exhibits more stable at high temperature with higher content of HPPs. Meanwhile, the HPPs with higher contents are more stable at high temperature and yield more char after degradation, because the crosslinking carbonisation occurred during its decomposition and the char formed acted as a protective layer on the polymer surface against heat and oxygen diffusion [105]. Consequently, the high char yield limited the production of combustible gases, thus decreased the exothermicity of pyrolysis reaction and inhibited the thermal conductivity of the burning materials that weakened the flammability of the materials.

Hyperbranched polyphosphate ester (HPPE) and phenolic melamine (PM) were blended in different ratios with a commercial epoxy resin to obtain a series of flame retardant resins by Wang et al. [106]. The diglycidyl ether of bisphenol-A-BPA_{100} (WSR618-BPA_{100}) does not contain any flame-retardant components, began to lose its weight at about 300°C, and degrades almost completely below 620°C. However, epoxy resins containing phosphorus components, WSR-$HPPE_{100}$ and WSR-PM_{50}/$HPPE_{50}$, still had char yields at over 900°C. In a word, epoxy resins containing a higher percentage of HPPE exhibited relatively lower thermostability at lower temperature while higher thermostability and higher efficiency in char formation at elevated temperature.

A new type of hyperbranched polyphosphamide (HBPPA-Si) was synthesized using phosphorus trichloride (POCl 3), 4,4 ′- diaminodiphenylmethane(DDM) and (3-aminopropyl) triethoxysilane (APTES) as raw materials by Chen et al. [107]. By incorporating 25 wt% of APP and HBPPA-Si with an optimum mass ratio of 1:1 into polypropylene (PP) composites, which have higher flame retardancy and smoke suppression properties. Figure 14 is synthetic route and structure of HBPPA-Si.

A series of hyperbranched poly phosphate ammonium polyphosphate salts (HBPOPNs) with different generations of hydroxyl terminated hyperbranched polymers (HBPs) were successfully prepared by modifying them. The results showed that the peak heat release rate and total heat release of treated samples decrease slightly with the increase of the number of generations. The second to fourth generation hyperbranched polymers can be used in cotton fabrics, exhibiting excellent flame retardancy and durability **[**108**]**. Figure 15 is Flame-retardant finishing of cotton fabrics.

The limited oxygen index (LOI) value can be used as an indicator to evaluate flame retardancy of a polymer. A higher LOI value is obtained with higher phosphorus content of HPPs in polymers. When HPPE blended with BPA, it increased drastically from 23 to 27 by the incorporation of 25 wt % HPPE in the curing agent complex. The same with the TGA, the char layers had been formed, and the larger the degree of expansion and the thicker the insulating layer would be formed to protect the underlying material, and thus the higher the LOI value is.

The flame retardants containing phosphorus and nitrogen generally possess a synergistic effect between phosphorus and nitrogen as they are burning [109,110]. HPPs exhibit higher hydrolytic stability than polyphosphates due to the partly hydrolysable P-O-C bond substituted by P-N bond [111,112]. Moreover, it was reported that phosphoramide structure could be more effective than phosphate structure in promoting the char formation and reducing the pyrolysis gases [113]. Li et al. [114] synthesized the intumescent flame retarded acrylonitrile-butadiene-styrene (IFR-ABS) with hyperbranched polyamine charring agent (HPCA) and ammonium polyphosphate (APP) via melt blending. The LOI for IFR-ABS is improved to 26.9 from 18.0 for ABS. The further degradation of ABS has been weakened. The IFR-ABS with suitable APP/HPCA ratio can form excellent and compact carbonaceous residues containing P-O-C structure, which hinder the transfer of heat flow and combustible gas and thus good flame retardance is obtained. Figure 16 is the degradation process of APP/HPCA and IFR-ABS.

4.3 Coatings

Hyperbranched polymers show structural characters and physical properties and much more accessible synthetically. Researchers have demonstrated that some hyperbranched polymers have superior photosensitivity and higher overall properties of hardness, flexibility, and adhesion force and impact strength [115]. The features of HPPs are also very favorable in coating applications, and the most prominent use of HPPs is as the reactive multifunctional components in coatings and resin formulations.

However, most conventional coatings are flammable, which demands the development of flame-retardant systems to reduce the fire hazards for some applications, such as the matrix for optical fibers [116] and wood coatings. HPPs applied in the coatings can improve the flame resistance. Among the phosphorus-based fire retardants, phosphorus-nitrogen synergistic combination is a more promising system and may be proceeding in this direction. The viscosity of HPPs is considered as one of the most important parameters as it affects its flow ability, air release rate and photopolymerization rate, and the final properties of the cured film.

UV-curable coatings represent a class of coatings with no or low volatile organic compounds, offering many advantages such as fast drying, broad-formulating range, reduced energy consumption, and low space and capital requirement for curing equipment [117]. HPPs with acrylate, vinyl ether, and epoxy functions have been used as a multifunctional crosslinker in coatings with UV curing methods. Coatings containing HPPs exhibit excellent flame retardation and low viscosity, and the UV-cured films have remarkable tensile strength, elongation at break, and good toughness. An efficient and green UV curing strategy is proposed to achieve strong, flexible and transparent urethane polyacrylate coatings based on acrylic-terminated hyperbranched polyurethane (AHPU) (Figure 17) [118].

HPPA was blended with TAEP in different ratios to obtain a series of UV-curable resins to find the thermal degradation mechanism of their cured films in air. The final unsaturation conversion (P_f) after a given irradiation

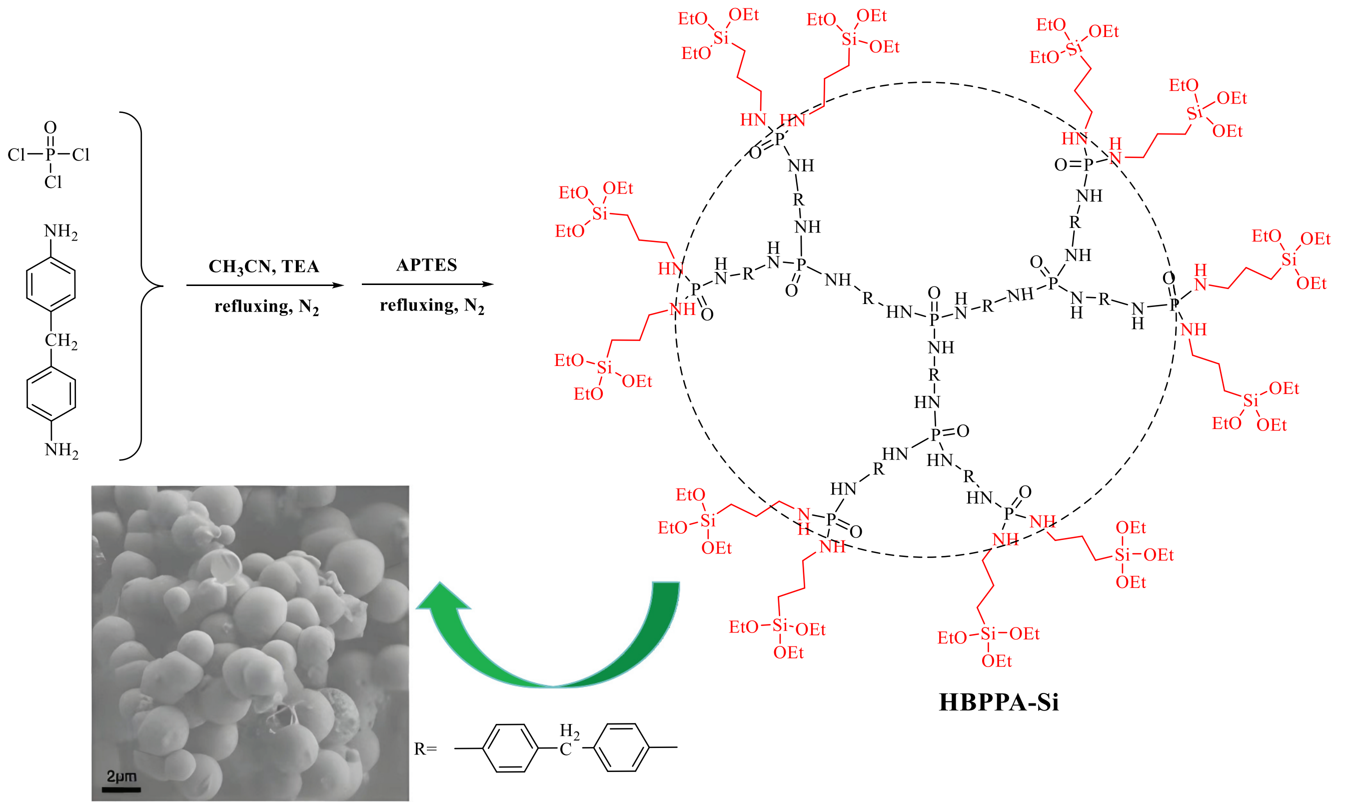


Figure 14. Synthetic route and structure of HBPPA-Si [107].

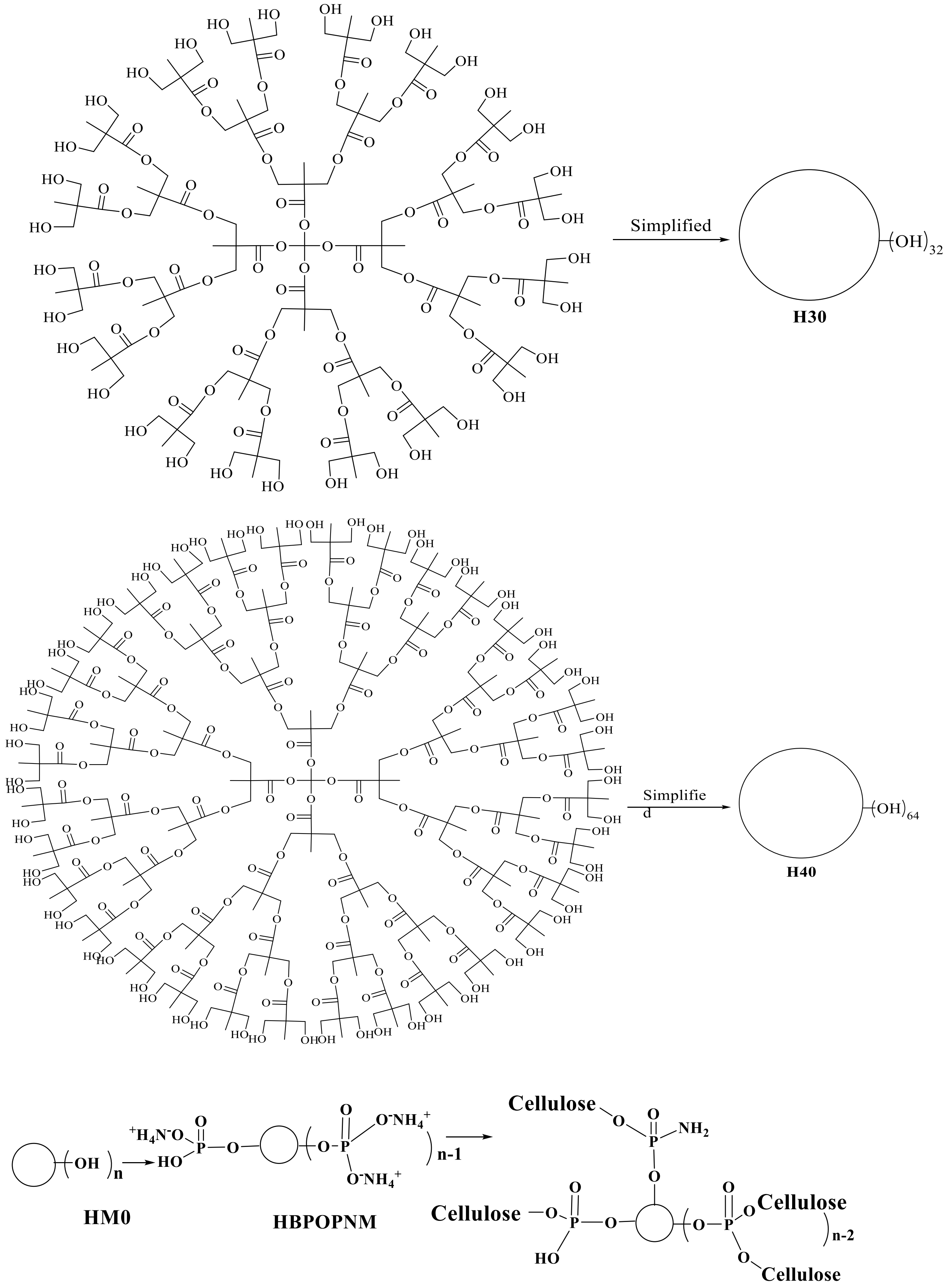


Figure 15. Flame-retardant finishing of cotton fabrics [108].

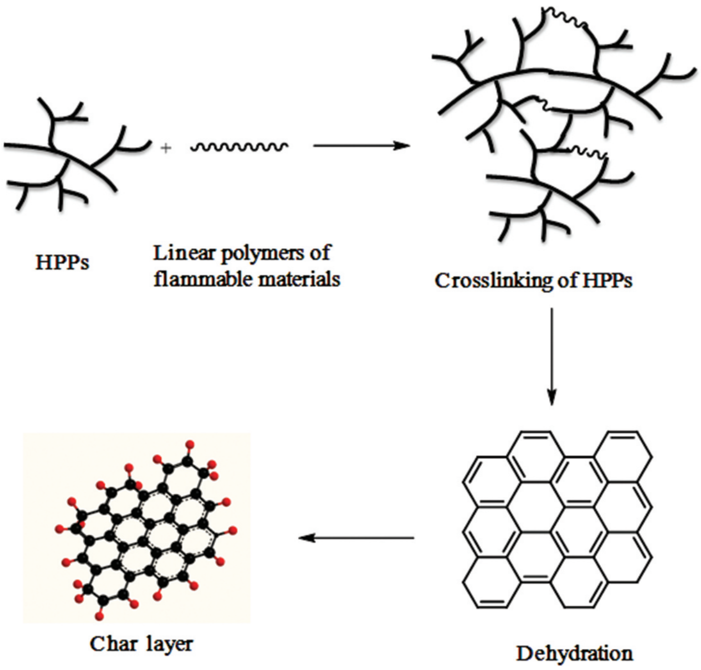


Figure 16. The degradation process of HPPs and IFR-ABS [114].

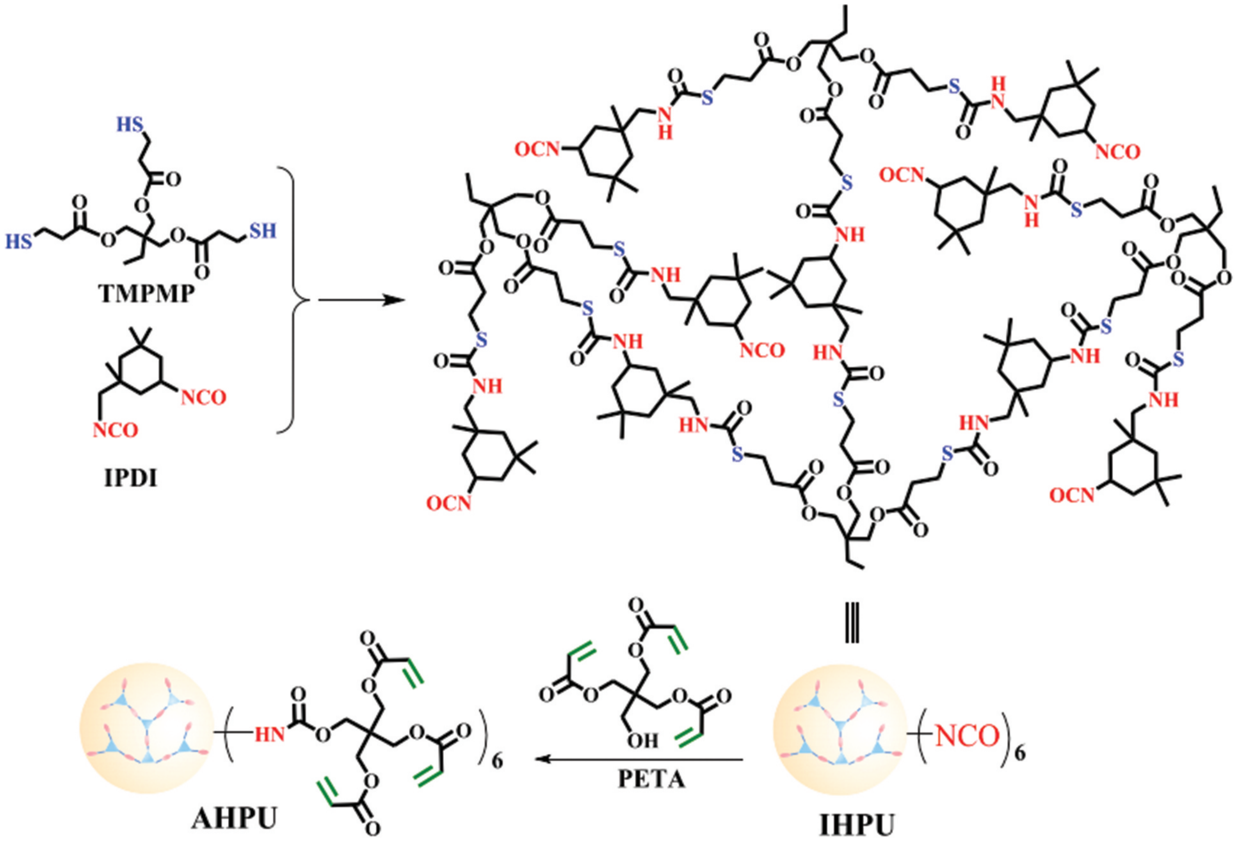


Figure 17. Synthesis scheme of IHPU and AHPU [118].

time increases linearly from 66.9% to 82.1% with increasing HPPA content, which is due to the fact that HPPA has much longer spacer chain than TAEP. The crosslinking density and T_g of the cured film decrease along with the content of HPPA in the blend. The toughness of TAEP is improved by the addition of HPPA from 13.1 to 26.1 MPa, and an elongation at break two times of that for cured TAEP. Furthermore, less than 20% HPPA addition improved both the tensile strength and elongation at break without damaging the modulus. Moreover, it was found that the flame retardancy of HPPA mainly acting in the condensed phase and the gas-phase mechanism holds the dominant effect as their blends are burning, the expanding charred crusts were formed after the TAEP/HPPA blends burned, and the degree of expansion increases with the HPPA content increasing.

4.4 Biomedical materials

Hyperbranched polymers have been used as the base for drug delivery and compared to the amphiphilic linear copolymers, amphiphilic-hyperbranched polymers have demonstrated some unique characteristics, such as structural diversities, special self-assembly mechanism, smart responses and facile functionalization [119,120]. These properties make amphiphilic hyperbranched polymers very useful to construct promising drug delivery systems with improved micellar stability and drug loading ability [121–123]. HPPs have the peculiar performances due to phospholipids as a well-known class of blood compatible and non-cytotoxic amphiphilic biomolecules containing a hydrophilic phosphate ester headgroup and two hydrophobic aliphatic chains [124]. Li et al. [125] designed a redox reactive hyperbranched polymer prodrug (HBPP) with a high drug content of 62.0%, and the single-molecule micelle of the hyperbranched polymer prodrug (HBPP) showed good tumor selective drug release. Figure 18 shows the application of hyperbranched polymers in prodrugs.

In order to study the ability of drug delivery, the structures and size of the micellar would be observed by TEM and detected by DLS. As for amphiphilic HPPs, most of them would spontaneously self-assemble into multimolecular micelles driven by the strong hydrophobic interactions of the hydrophobic macromolecules, whereas the hydrophilic polyphosphate maintains a hydration barrier to provide stability to the micelle in the water. The diameter of HPPs investigated by DLS and TEM. The micelles by TEM image were much smaller than the D_h measured by DLS. This may be related to the degree of hydration and polydispersity effects, and the mean diameter determined by TEM compared reasonably well to the hydrodynamic diameter.

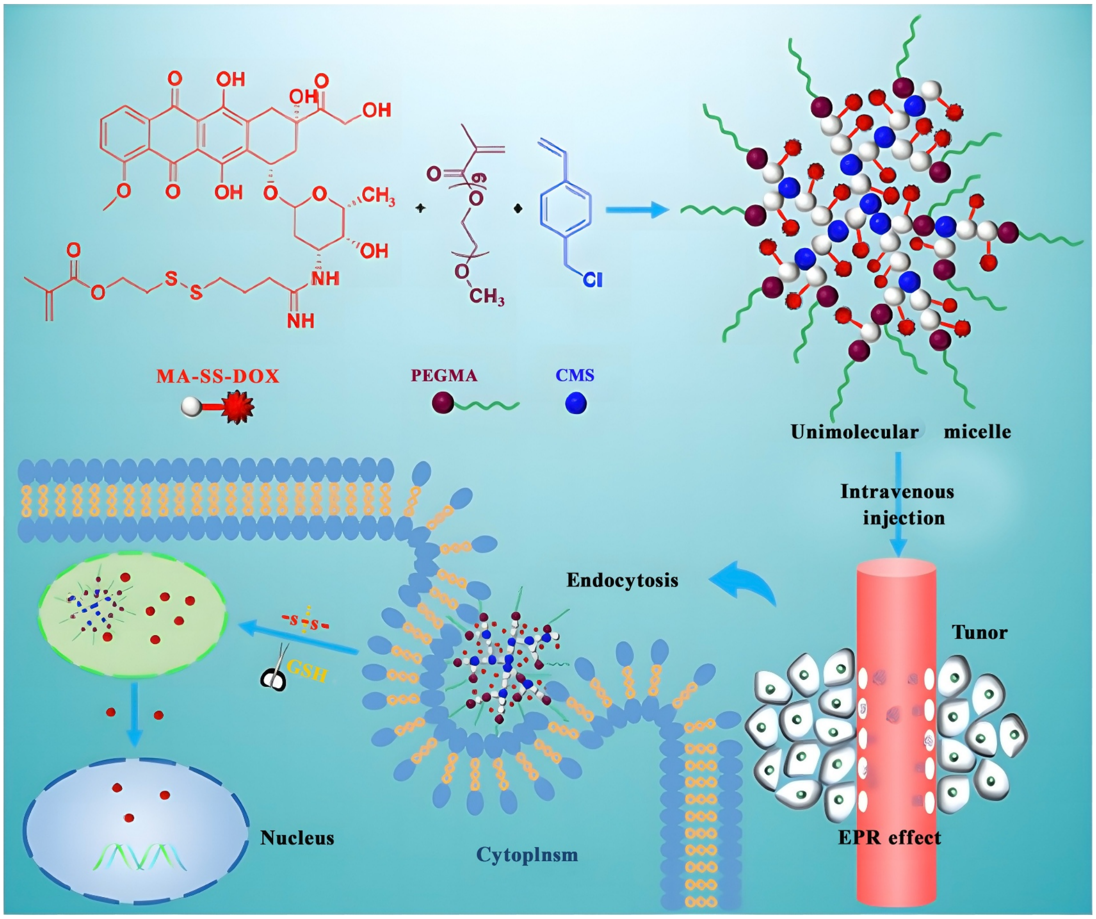


Figure 18. Synthesis and application of hyperbranched polymer prodrugs (HBPP) [125].

The multimolecular micelles are a kind of multimicelle aggregate (MMA) with building blocks of small micelles or unimolecular micelles [126]. For the size of micelle, the small micelles are beneficial to carry colloidal drug to our system [127,128], such as, maintaining a lower level of reticuloendothelial system (RES) uptake, minimal renal excretion, and the ability to take advantage of the EPR effect for passive tumor targeting [129].

The characteristic size and morphology of self-assembled H40-*star*-(PLA-b-PEP-OH) micelles were determined by DLS and TEM by Liu et al. (Figure 19) [75]. The size distribution curve of the micelles in aqueous solution displays a monomodal distribution with a hydrodynamic diameter of 130 ± 60 nm. A TEM microscope shows that H40-*star*-(PLA-*b*-PEP-OH) aggregates into approximately spherical micelles in water. The result indicates that the size of H40-*star*-(PLA-*b*-PEP-OH) micelles is benefit for drug delivery.

The researches of vitro cytotoxicity, drug loading, and intracellular drug delivery are other important methods for drug delivery. The redox-responsive polyphosphate nanosized assemblies based on amphiphilic hyperbranched multiarm copolyphosphates (HPHSEP-*star*-PEP$_x$) were synthesized by Liu et al. [130]. The HPHSEP-*star*-PEP$_x$ could self-assemble into spherical micellar nanoparticles in aqueous media with tunable size from about 70 to 100 nm via adjusting the molecular weight of PEP multiarm. Furthermore, the glutathione-mediated intracellular drug delivery was investigated against a HeLa human cervical carcinoma cell line, and the results indicate that doxorubicin-loaded (DOX-loaded) HPHSEP-*star*-PEP$_x$ micelles showed higher cellular proliferation inhibition against glutathione monoester pretreated HeLa cells than that of the nonpretreated ones. Liu et al. [131] synthesized biodegradable micelles for glutathione-mediated intracellular drug delivery was developed on the basis of an amphiphilic hyperbranched multiarm copolymer (H40-*star*-PLA-SS-PEP). The H40-*star*-PLA-SS-PEP contains hydrophilic shell with the disulfide linkage and hydrophobic polyester and was able to self-assemble into micelles in aqueous solution with an average diameter of 70 nm. The average diameter of micelles was increased rapidly and further resulted in the formation of microsized particles or even severe aggregations, because of the detachment of the hydrophilic shell and the enhancement of hydrophobic interaction of the polyester inner core.

A novel amphiphilic photo-degradable hyperbranched polymer was reported by Jin et al. [132]. Firstly, the hyperbranched o-nitrobenzyl containing poly(amino ester)s (HPAE) were prepared by one-pot Michael addition polymerization. Then, the bioinspired phosphorylcholine grafted the HPAE (HPAE-PC) was synthesized via thiol-ene click chemistry. The bioinspired phosphorylcholine provided a potential strategy for the surface tailoring of micelles. The micellar aggregates were observed by DLS. The intensity average hydrodynamic diameter (D_h) of the micelles was 117.5 nm with a polydispersity index of 0.286. The morphology of the micelles was spherical with mean diameter of about 90 nm by TEM, which was much smaller than the D_h measured by DLS (117.5 nm). HPAE-PC micelles were used to load anticancer drug Doxorubicin (DOX), and the DOX-loaded micelles exhibited faster drug release in A549 cells after UV irradiation. They proved that novel amphiphilic photo-degradable hyperbranched polymers can be used to construct spatiotemporal on-demand drug delivery system for cancer therapy.

Bai et al. [133] synthesized a series of hyperbranched polyphosphates without any large conjugated π bonds (HPPE) using triethyl phosphate and 1,3-propanediol as raw materials via a facile one-pot nucleophilic

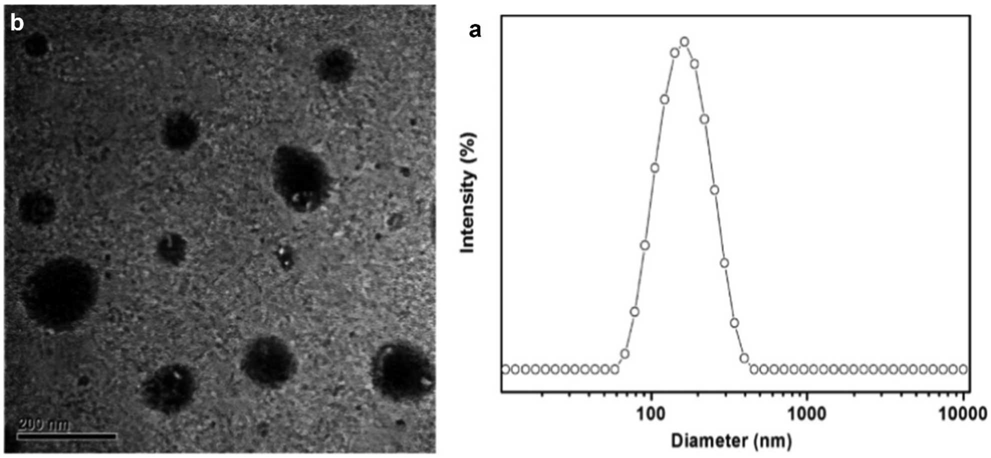


Figure 19. The characteristic size and morphology of self-assembled H40-star-(PLA-b-PEP-OH) micelles [75].

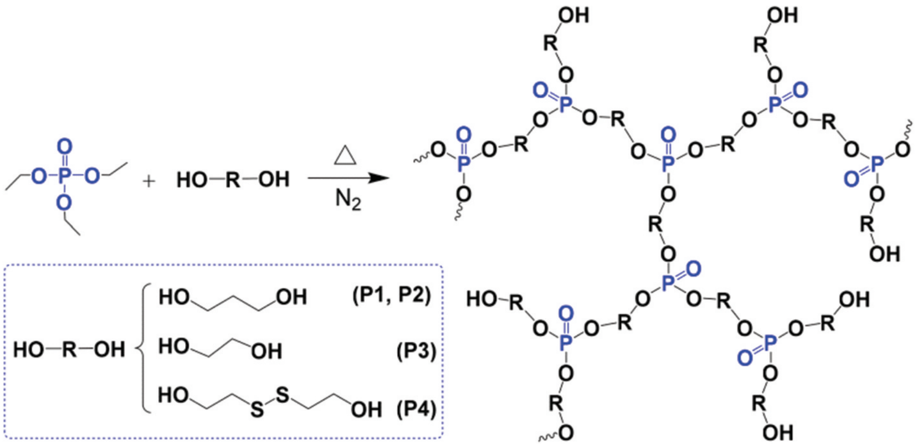


Figure 20. Synthesis route of the hyperbranched polyphosphate [133].

substitution reaction. Experimental studies had shown that HPPE doped PVA films could produce blue room temperature phosphorescence due to its enhanced rigidity and exhibit excellent selectivity in Fe^{3+} sensing. Figure 20 shows the synthesis route of the hyperbranched polyphosphate.

It is reported that polyphosphate (PPE) has been used in (bone) tissue engineering due to its excellent bioavailability and good physicochemical properties. Besides, PPE nanoparticles adhere to the surface of bones model, this proved that it has potential for bone adhesion. As a consequence, PPE has emerged good applicable future in bone regeneration, and a lot of research has focused on developing polyphosphate scaffolds for bone tissue regeneration [134,135].

5. Conclusions

The many properties of hyperbranched polymers, such as good solubility, low viscosity and multi-functionality at end groups, are generally inherited. HPPs as the part of hyperbranched polymers also play important roles in applications. Recently, HPPs can be synthesized by polycondensation of AB_2 type monomers, $A_2 + B_3$ monomers, A_2+ BB'_2 monomers, and A_3+ BB′ monomers and also can be obtained without phosphate as monomer. HPPs can be modified or functionalized by end capping and hypergrafting to improve the performances. Due to the outstanding properties of HPPs and their derivatives, they are potentially useful in the areas of polymer blends, coatings, leather, flame retardant, and drug delivery. Because the properties of hyperbranched polymers such as solubility, polarity, capacity, crystallinity, chain entanglement, viscosity, virulence, thermal stability as well as rigidity (glass transition temperature) can be tailored. Besides, HPPs exhibit potential and important application value in the biomedical field, such as drug delivery, bone regeneration and other bioengineering, even extended to many fields such as medical products, nanomaterials, aerospace devices, etc. In the future research, as our expectation, the materials and devices though using the potential HPPs will be successfully developed in the future.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

References

[1] Zhu SS, Zhao MJ, Zhou HG, et al. One-pot synthesis of hyperbranched polymers via visible light regulated switchable catalysis. Nat Commun. 2023;14(1):1622.

[2] Ling C, Guo LM. Recent developments and applications of hyperbranched polymers as flame retardants. J Anal Appl Pyrol. 2023;169:105842.

[3] Chen Y. Study on synthesis and properties of hyperbranched-polystyrene-based and hyperbranched polyethylene-based-polymers. Zhe jiang: Zhe jiang University; 2016.

[4] Zhu TY, Lu CX, Lu XX, et al. Interfacial and tensile properties improvement of composites using a modified matrix with epoxy-terminated hyperbranched polyether sulfone. J Appl Polym Sci. 2022;139(46):e53169.

[5] Pastor-Pérez L, Barriau E, Berger-Nicoletti E, et al. Incorporation of a photosensitizer core within hyperbranched polyether polyols: effect of the branched shell on the core properties. Macromolecules. 2008;41 (4):1189–1195.

[6] Chen GH, Ye L, Zhang K, et al. Hyperbranched polyether boosting ionic conductivity of polymer electrolytes for all-solid-state sodium ion batteries. Chem Eng J. 2020;394:124885.

[7] Liu C, Ran X, Li G, et al. Facile-synthesis and shape-adjustment of irregular gravel-like PtPd nanocatalysts by three-dimensional hyperbranched polyamide (HBPA) with enhanced activity in ethanol oxidation. Int J Hydrogen Energ. 2023;48(57):21686–21700.

[8] Zhao L, Zhu H, Tian GL, et al. A novel hyperbranched polyethyleneimine–graphene composite as shale inhibitor for drilling fluid. RSC Adv. 2023;13(4):2611–2619.

[9] Ohta Y, Huang CF, Lee YH, et al. Synthesis of well-defined block copolymers of hyperbranched polyamide and polystyrene and their micelle-to-vesicle transformation in organic solvents. Macromol Chem Phys. 2023;224 (1):2200298.

[10] Jin T, Zeng HY, Huang YF, et al. Bio-hyperbranched polyesters synthesized from citric acid and bio-polyols and applications on wood adhesives. Polym Test. 2023;120:107974.

[11] Gunasekhar R, Prabu AA. Polyvinylidene fluoride/aromatic hyperbranched polyester 2nd generation based triboelectric sensor for polysomnographic and health monitoring applications. Sens Actuat A Phys. 2023;355:114311.

[12] Sun J, Hong YL, Fang XQ, et al. Fluorescent phosphine oxide-containing hyperbranched polyesters: design, synthesis and their application for Fe^{3+} detection. J Mater Chem C. 2023;11(5):1927.

[13] Nabae Y, Tomita M, Taniguchi T, et al. Hyperbranched vs. linear polymers in the catalysis by sulfonic acid functionalized poly(ether sulfone). Polymer. 2018;137:324–329.

[14] Saia SM, Carrick HJ, Buda AR, et al. Critical review of polyphosphate and polyphosphate accumulating organisms for agricultural water quality management. Environ Sci Technol. 2021;55(5):2722–2742.

[15] Guo LL, Yan L, He YY, et al. Hyperbranched Polyborate: a non-conjugated fluorescent polymer with unanticipated high quantum yield and multicolor emission. Angew Chem Int Ed. 2022;61(29):e202204383.

[16] Zhang T, Howell BA, Zhang D, et al. Hyperbranched poly (ester) s for delivery of small molecule therapeutics. Polym Adv Technol. 2018;29(8):2352–2363.

[17] Liu J, Huang W, Yan D. Hyperbranched polyphosphates and their biomedical applications. Nanomed-Nanotechnol. 2016;2(12):466–575.

[18] Liu JY, Huang W, Pang Y, et al. Hyperbranched polyphosphates: synthesis, functionalization and biomedical applications. Chem Soc Rev. 2015;44(12):3942–3953.

[19] Xu ZS, Liu DL, Yan L, et al. Synergistic effect of sepiolite and polyphosphate ester on the fire protection and smoke suppression properties of an amino transparent fire-retardant coating. Prog Org Coat. 2020;141:105572.

[20] Zhu CJ, He MS, Cui JG, et al. Synthesis of a novel hyperbranched and phosphorus-containing charring-foaming agent and its application in polypropylene. Polym Adv Technol. 2018;29(9):2449–2456.

[21] Hao YX, Zhong LY, Li TC, et al. High-performance recyclable and malleable epoxy resin with vanillin-based hyperbranched epoxy resin containing dual dynamic bonds. ACS Sustain Chem Eng. 2023;11(30):11077–11087.

[22] Cuneo T, Gao HF. Recent advances on synthesis and biomaterials applications of hyperbranched polymers. Wires Nanomed Nanobi. 2020;12(6):e1640.

[23] Zhang XL. Hyperbranched aromatic polyesters: from synthesis to applications. Prog Org Coat. 2010;69 (4):295–309.

[24]. Kricheldorf H, Penczek S SP. Models of biopolymers by ring-opening polymerization. CRC press;1990. p. 160–225.

[25] Chen DP, Wang J. Synthesis and characterization of block copolymer of polyphosphoester and Poly(ε-caprolactone). Macromolecules. 2006;39(2):473–475.

[26] Xiao CS, Wang YC, Du JZ, et al. Kinetics and Mechanism of 2-Ethoxy-2-oxo-1,3,2-dioxaphospholane polymerization initiated by stannous octoate. Macromolecules. 2006;39(20):6825–6831.

[27] Gao C, Zheng X. Facile synthesis and self-assembly of multihetero-arm hyperbranched polymer brushes. Soft Matter. 2009;5(23):4788–4796.

[28] Malmström E, Johansson M, Hult A. Hyperbranched aliphatic polyesters. Macromolecules. 1995;28(5):1698–1703.

[29] Hawker C, Lee R, Fréchet J. One-step synthesis of hyperbranched dendritic polyesters. J Am Chem Soc. 1991;113 (12):4583–4588.

[30] Segawa Y, Higashihara T, Ueda M. Hyperbranched polymers with controlled degree of branching from 0 to 100%. J Am Chem Soc. 2010;132(32):11000–11001.

[31] Liu JY, Huang W, Zhou YF, et al. Synthesis of hyperbranched polyphosphates by self-condensing ring-opening polymerization of HEEP without Catalyst. Macromolecules. 2009;42(13):4394–4399.

[32] Sun HL, Meng FH, Cheng R, et al. Reduction-sensitive degradable micellar nanoparticles as smart and intuitive delivery systems for cancer chemotherapy. Expert Opin Drug Deliv. 2013;10:1109–1122.

[33] Shibasaki Y, Sasahara R, Hoshino Y, et al. Reactivity-controlled synthesis of $A_2 + B_3$ type soluble hyperbranched polymers from aromatic diamines and cyanuryl chloride via a coupled monomer method. Mater Today Commun. 2020;24:101043.

[34] Shibasaki Y, Sasahara R, Hoshino Y, et al. Reactivity-controlled synthesis of $A_2 + B_3$ type soluble hyperbranched

polymers from aromatic diamines and cyanuryl chloride via a coupled monomer method. Mater Today Commun. 2020;24:101043.

[35] Flory P. Molecular size distribution in three dimensional polymers V. Post-gelation relationships. J Am Chem Soc. 1947;69(1):30–35.

[36] Cheng KC, Cheng PS, Wang PC. Hyperbranched polyurethane acrylates synthesized via copolymerization of monomers A_2 and B_3 with monofunctional compound BR added gradually at different rates. Polym Eng Sci. 2020;60(6):1138–1145.

[37] Kudo R, Tsukamoto T, Nakajo S, et al. Synthesis of A_2+B_3 type hyperbranched poly(amide-ether) block copolymer and its shape memory function. Eur Polym J. 2021; 146:110255.

[38] Zamboulis A, Nakiou EA, Christodoulou E, et al. polyglycerol hyperbranched polyesters: synthesis, properties and pharmaceutical and biomedical applications. Int J Mol Sci. 2019;20(24):6210.

[39] Yuan MJ, Wang S, Li GX, et al. UV curable hyperbranched polyester polyurethane acrylate for hydraulic machinery coating. Mater Res Express. 2021;8(3):035104.

[40] Huang ZG, Shi WF. Synthesis and properties of a novel hyperbranched polyphosphate acrylate applied to UV curable flame retardant coatings. Eur Polym J. 2007;43 (4):1302–1312.

[41] Wang QF, Shi WF. Synthesis and thermal decomposition of a novel hyperbranched polyphosphate ester used for flame retardant systems. Polym Degrad Stabil. 2006;91 (6):1289–1294.

[42] Wang HL, Wang QF, Huang ZG, et al. Synthesis and thermal degradation behaviors of hyperbranched polyphosphate. Polym Degrad Stabil. 2007;92(10):1788–1794.

[43] Liu JY, Pang Y, Chen J, et al. Hyperbranched polydiselenide as a self assembling broad spectrum anticancer agent. Biomaterials. 2012;33(31):7765–7774.

[44] Emrick T, Chang H, Fréchet JMJ. The preparation of hyperbranched aromatic and aliphatic polyether epoxies by chloride-catalyzed proton transfer polymerization from ABn and A_2+B_3 monomers. J Polym Sci Pol Chem. 2000;38(S1):4.850–4869.

[45] Ma N, Li Y, Xu HP, et al. Dual redox responsive assemblies formed from diselenide block copolymers. J Am Chem Soc. 2010;132(2):442–443.

[46] Zhang X, Xu HP, Dong ZY, et al. Highly efficient dendrimer-based mimic of glutathione Peroxidase. J Am Chem Soc. 2004;126(34):10556–10557.

[47] Lee SC, Min BG. Depression of glass transition temperature due to the chain extension in glassy state. Polymer. 1999;40(19):5445–5448.

[48] Li XJ, Zhang SL, Wang H, et al. Facile synthesis and characterization of hyperbranched poly(aryl ether ketone)s obtained via an A2+BB′2 approach. Polym Int. 2010;59(10):1360–1366.

[49] Han B, Sun D, Li XJ, et al. Preparation and characterization of hyperbranched poly(ether sulfone) and its application as a coating additive for linear poly(ether sulfone). J Appl Polym Sci. 2016;133(36):43892.

[50] He LB, Wang T, Liu XC, et al. Synthesis and properties of a novel multifunctional hyperbranched polyamide. J Polym Res. 2013;20(8):1–8.

[51] Wang HL, Xu SP, Shi WF. Photopolymerization behaviors of hyperbranched polyphosphonate acrylate and properties of the UV cured film. Prog Org Coat. 2009;65 (4):417–424.

[52] Li Z, Wei P, Yang Y, et al. Synthesis of a hyperbranched poly (phosphamide ester) oligomer and its high-effective flame retardancy and accelerated nucleation effect in polylactide composites. Polym Degrad Stabil. 2014;110:104–112.

[53] Huang Z, Rao SH, Fan WJ, et al. A supramolecular hyperbranched polymer constructed by the host-guest interaction and complementary metal-coordination interaction. Polym Chem. 2022;13(40):5775–5780.

[54] Kobayashi N, Kijima M. Microporous materials derived from two-and three-dimensional hyperbranched conjugated polymers by thermal elimination of substituents. J Mater Chem. 2007;17(40):4289–4296.

[55] Chen SF, Zhang DH, Cheng XJ, et al. Preparation and characterization of a novel hyperbranched polyphosphate ester. Mater Chem Phys. 2012;137(1):154–159.

[56] Hawker CJ, Fréchet JMJ. Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules. J Am Chem Soc. 1990;112(21):7638–7647.

[57] Yan DY, Müller AHE, Matyjaszewski K. Molecular parameters of hyperbranched polymers made by self-condensing vinyl polymerization. 2. degree of branching. Macromolecules. 1997;30(23):7024–7033.

[58] Thilo E. Angew. Chem Int Ed. 1965;4(12):1061–1071.

[59] Lovas M, Tanka-Salamon A, Beinrohr L, et al. Polyphosphate nanoparticles enhance the fibrin stabilization by histones more efficiently than linear polyphosphates. PLOS One. 2022;17(4):e0266782.

[60] Yang XZ, Wang YC, Tang LY, et al. Synthesis and characterization of amphiphilic block copolymer of polyphosphoester and poly(L-lactic acid). J Polym Sci Chem. 2008;46(19):6425–6434.

[61] Nifant'ev IE, Shlyakhtin AV, Tavtorkin AN, et al. Mechanistic study of transesterification in TBD-catalyzed ring-opening polymerization of methyl ethylene phosphate. Eur Polym J. 2019;118:393–403.

[62] Fan JK, Ren N, Zhang CY, et al. Synthesis of hyperbranched polyolefin with well-defined terminal functional group. Polymer. 2022;242:124571.

[63] Li J, Liu P. Facile synthesis of a hyperbranched polymer prodrug as unimolecular micelles for overcoming multidrug resistance. Polym Chem. 2022;13(10):1369–1375.

[64] Padilla-Coley S, Xu H, Morsby J, et al. Supramolecular loading of a broad spectrum of molecular guests in hyperbranched polytriazole nanoparticles with cores containing multiple functional groups. Biomacromolecules. 2020;21(6):2165–2175.

[65] Iwasaki Y. Bone mineral affinity of polyphosphodiesters. Molecules. 2020;25(3):758.

[66] Gu JT, Jiao K, Li, et al. Polyphosphate-crosslinked collagen scaffolds for hemostasis and alveolar bone regeneration after tooth extraction. Bioact Mater. 2022;15:68–81.

[67] Yu QY, Liang XY, Rao Q, et al. Characterization of open chromatin in response to cold reveals transcription factor association with preferred binding distances in cassava. Ind Crop Prod. 2023;202:117080.

[68] Tang LY, Wang YC, Li Y, et al. Shell-detachable micelles based on disulfide-linked block copolymer as potential carrier for intracellular drug delivery. Bioconjugate Chem. 2009;20(6):1095–1099.

[69] Cheng J, Ding JX, Wang YC, et al. Synthesis and characterization of star-shaped block copolymer of poly-(ε-caprolactone) and poly(ethyl ethylene phosphate) as drug carrier. Polymer. 2008;49(22):4784–4790.

[70] Liu JY, Huang W, Pang Y, et al. Self-assembled micelles from an amphiphilic hyperbranched copolymer with polyphosphate arms for drug delivery. Langmuir. 2010;26(13):10585–10592.

[71] Liu J, Pang Y, Zhu Z, et al. Therapeutic nanocarriers with hydrogen peroxide-triggered drug release for cancer treatment. Biomacromolecules. 2013;14(5):1627–1636.

[72] Jie D, Chen XT, Li YQ, et al. Study on the hyperbranched polyphosphate ester modified epoxy resin. J Tianjin Univ Sci Technol. 2010;6:30–38.

[73] Wang XY, Deng HM, Li J, et al. A neutral supramolecular hyperbranched polymer fabricated from an AB_2-Type Copillar[5]arene. Macromol Rapid Comm. 2013;34(23–24):1856–1862.

[74] Li SP, Cui C, Hou HJ. Synthesis and characterization of amino-terminated hyperbranched polymer and its effect on impact resistance of epoxy resin thermosets. Colloid Polym Sci. 2015;293(9):2681–2688.

[75] Zhang D, Wang J, Li T, et al. Synthesis and characterization of a novel low-viscosity unsaturated hyperbranched polyester resin. Chem Eng Technol. 2011;34(1):119–126.

[76] Gunasekhar R, Indumathy B, Sathiyanathan P, et al. A mini-review on the synthesis, characterization and applications of end-capped hyperbranched polymers. ECS Trans. 2022;107(1):11351–11360.

[77] Wei H, Cheng SX, Zhang XZ, et al. Thermo-sensitive polymeric micelles based on poly(N-isopropylacrylamide) as drug carriers. Prog In Polym Sci. 2009;34(9):893–910.

[78] Mao J, Ni PH, Mai YY, et al. Multicompartment micelles from hyperbranched star-block copolymers containing polycations and fluoropolymer segment. Langmuir. 2007;23(9):5127–5134.

[79] Liu JY, Huang W, Pang Y, et al. The in vitro biocompatibility of self-assembled hyperbranched copolyphosphate nanocarriers. Biomaterials. 2010;31(21):5643–5651.

[80] Vlassiouk I, Park CD, Vail SA, et al. Control of nanopore wetting by a photochromic spiropyran: a light-controlled valve and electrical switch. Nano Lett. 2006;6(5):1013–1017.

[81] Chen CJ, Jin Q, Liu GY, et al. Reversibly light-responsive micelles constructed via a simple modification of hyperbranched polymers with chromophores. Polymer. 2012;53(17):3695–3703.

[82] Liu JY, Pang Y, Huang W, et al. Self-assembly of phospholipid-analogous hyperbranched polymers nanomicelles for drug delivery. Biomaterials. 2010;31(6):1334–1341.

[83] Kwon G, Naito M, Yokoyama T, et al. Micelles based on AB block copolymers of poly(ethylene oxide) and poly(.beta.-benzyl L-aspartate). Langmuir. 1993;9(4):945–949.

[84] Cheng HX, Wang SG, Yang JT, et al. Synthesis and self-assembly of amphiphilic hyperbranched polyglycerols modified with palmitoyl chloride. J Colloid Interface Sci. 2009;337(1):278–284.

[85] Schmaljohann D, Häußler L, Pötschke P, et al. Modification with alkyl chains and the influence on thermal and mechanical properties of aromatic hyperbranched polyesters. Macromol Chem Phys. 2000;201(1):49–57.

[86] Xia L, Zhou ZP. Preparation and characterization of the composite materials of SiO_2-multi-arms star hyperbranched block copolymer. Funct Mater. 2014;45:2090–2094.

[87] Yan DF. Nanomed. Nanotech Biol Med. 2016;2(2):466.

[88] Cappella B, Kaliappan SK. Determination of thermomechanical properties of a model polymer blend. Macromolecules. 2006;39(26):9243–9252.

[89] Xu PJ, Du XM, Cong PL, et al. Road Mater. Pavement. 2022;23(1):234–246.

[90] Yang G, Fu SY, Yang JP. Preparation and mechanical properties of modified epoxy resins with flexible diamines. Polymer. 2007;48(1):302–310.

[91] Asif A, Huang CY, Shi WF. Photopolymerization of waterborne polyurethane acrylate dispersions based on hyperbranched aliphatic polyester and properties of the cured films. Colloid Polym Sci. 2005;283(7):721–730.

[92] Jeng RJ, Wang JR, Lin JJ, et al. Flame retardant epoxy polymers using phosphorus-containing polyalkylene amines as curing agents. J Appl Polym Sci. 2001;82(14):3526–3528.

[93] Huang ZG, Shi WF. UV curing behavior of hyperbranched polyphosphate acrylate/di (hydroxylpropyl methacrylate) piperazine and properties of the cured film. Prog Org Coat. 2007;59(4):312–317.

[94] Fang KY, Li J, Ke CH, et al. Promotion effect of a hyperbranched polyphosphate ester flame retardant on char formation of polyamide 6. Acta Polym Sin. 2011;1(1):55–62.

[95] Chen L, Wang YZ. Aryl Polyphosphonates: useful halogen-free flame retardants for polymers. Materials. 2010;3(10):4746–4760.

[96] Horacek H, Pieh S. The importance of intumescent systems for fire protection of plastic materials. Polym Int. 2000;49(10):1106–1114.

[97] Liu WC, Varley RJ, Simon GP. Phosphorus-containing diamine for flame retardancy of high functionality epoxy resins. Part II. The thermal and mechanical properties of mixed amine systems. Polymer. 2006;47(6):2091–2098.

[98] Levchik SV, Weil ED. A review of recent progress in phosphorus-based flame retardants. J Fire Sci. 2006;24:345–364.

[99] Qi HS, Liu SW, Chen XL, et al. The flame retardant and thermal performances of polypropylene with a novel intumescent flame retardant. J Appl Polym Sci. 2020;137(36):49047.

[100] Huang Z, Li SH, Tsai LC, et al. Flame retardant polypropylene with a single molecule intumescent flame retardant based on chitosan. Mater Today Commun. 2022;33:104689.

[101] Song YP, Wang DY, Wang XL, et al. A method for simultaneously improving the flame retardancy and toughness of PLA. Polym Adv Technol. 2011;22(12):2295–2301.

[102] Jin XD, Cui SP, Sun SB, et al. The preparation and characterization of polylactic acid composites with chitin-

based intumescent flame retardants. Polymers. 2021;13 (20):3513.

[103] Huang ZG, Shi WF. Thermal degradation behavior of hyperbranched polyphosphate acrylate/tri(acryloyloxyethyl) phosphate as an intumescent flame retardant system. Polym Degrad Stabil. 2007;92(7):1193–1198.

[104] Lin CH, Wang CS. Novel phosphorus-containing epoxy resins Part I. Synthesis and properties. Polymer. 2001;42 (5):1869–1878.

[105] Liu YL. Epoxy resins from novel monomers with a bis-(9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl-) substituent. J Polym Sci A Polym Chem. 2002;40(3):359–368.

[106] Wang QF, Shi WF. Kinetics study of thermal decomposition of epoxy resins containing flame retardant components. Polym Degrad Stabil. 2006;91(8):1747–1754.

[107] Chen XS, Ma YH, Cheng YJ, et al. Synergistic effect between a novel silane-containing hyperbranched polyphosphamide and ammonium polyphosphate on the flame retardancy and smoke suppression of polypropylene composites. Polym Degrad Stabil. 2020;181:109348.

[108] Ling C, Tan YZ, Wang YH, et al. Effect of treatment-varying generation number of with hyperbranched polyphosphate ammonium salts on the fire retardant finish performance of cotton fabric. Cellulose. 2021;28 (6):3823–3832.

[109] Weng SX, Li Z, Bo CY, et al. Design lignin doped with nitrogen and phosphorus for flame retardant phenolic foam materials. React Funct Polym. 2023;185:105535.

[110] Qin YL, Li MC, K TK, et al. A study on the modification of polypropylene by a star-shaped intumescent flame retardant containing phosphorus and nitrogen. Polym Degrad Stabil. 2022;195:109801.

[111] Joglekar M, Trewyn BG. Polymer-based stimuli-responsive nanosystems for biomedical applications. Biotechnol J. 2013;8(8):931–945.

[112] Brehme S, Schartel B, Goebbels J, et al. Phosphorus polyester versus aluminium phosphinate in poly(butylene terephthalate) (PBT): flame retardancy performance and mechanisms. Polym Degrad Stabil. 2011;96(5):875–884.

[113] Gaan S, Rupper P, Salimova V, et al. Thermal decomposition and burning behavior of cellulose treated with ethyl ester phosphoramidates: effect of alkyl substituent on nitrogen atom. Polym Degrad Stabil. 2009;94(7):1125–1134.

[114] Li J, Ke CH, Xu L, et al. Synergistic effect between a hyperbranched charring agent and ammonium polyphosphate on the intumescent flame retardance of acrylonitrile-butadiene-styrene polymer. Polym Degrad Stabil. 2012;97(7):1107–1113.

[115] Fu JC, Yu HJ, Wang, et al. Preparation and properties of UV-curable hyperbranched polyurethane acrylate hard coatings. Prog In Org Coat. 2020;144:105635.

[116] Hu X, Wang GJ, Huang Y. Study on the preparation and properties of novel transparent fire-resistive coatings. J Coat Technol Res. 2013;10(5):717–726.

[117] Cao HL, Chen C, Xie DB, et al. A hyperbranched amphiphilic acetal polymer for pH-sensitive drug delivery. Polym Chem. 2018;9(2):169–177.

[118] Czachor-Jadacka D, Pilch-Pitera B. Progress in development of UV curable powder coatings. Prog Org Coat. 2021;158:106355. doi:10.1016/j.porgcoat.2021.106355.

[119] Kavand A, Anton N, Vandamme T, et al. Synthesis and functionalization of hyperbranched polymers for targeted drug delivery. J Cont Release. 2020;321:285–311.

[120] Wu Y, Huang SM, Liu X, et al. Preparation of high-performance polyurethane-polyacrylate coatings based on hyperbranched structure and application in anti-ultraviolet film. Prog Org Coat. 2023;182:107614.

[121] Du WJ, Xu ZQ, Nyström AM, et al. 19 F-and fluorescently labeled micelles as nanoscopic assemblies for chemotherapeutic delivery. Bioconjugate Chem. 2008;19 (12):2492–2498.

[122] Bera S, Barman R, Ghosh S. Hyperbranched vs. linear poly (disulfide) for intracellular drug delivery. Polym Chem. 2022;13(36):5188–5192.

[123] Hu M, Chen MS, Li GL, et al. Biodegradable hyperbranched polyglycerol with ester linkages for drug delivery. Biomacromolecules. 2012;13(11):3552–3561.

[124] Yokoyama Y, Makino K, Terada H, et al. Phosphoric acid triester micelles: characterization and self-assembly. J Oleo Sci. 2023;72(10):969–977.

[125] Li J, Liu P. Facile synthesis of a redox-responsive hyperbranched polymer prodrug as a unimolecular micelle for the tumor-selective drug delivery. Bioconjugate Chem. 2022;33(2):411–417.

[126] Zhou YF, Yan DY. Supramolecular self-assembly of amphiphilic hyperbranched polymers at all scales and dimensions: progress, characteristics and perspectives. Chem Commun. 2009;10(10):1172–1188.

[127] Yokoyama M, Satoh A, Sakurai Y, et al. Incorporation of water-insoluble anticancer drug into polymeric micelles and control of their particle size. J Control Release. 1998;55(2–3):219–229.

[128] Balafouti A, Pispas S. P(OEGMA-co-LMA) hyperbranched amphiphilic copolymers as self-assembled nanocarriers. J Polym Sci. 2022;60(13):1931–1943.

[129] Schmalenberg K, Frauchiger L, Nikkhouy-Albers L, et al. Cytotoxicity of a unimolecular polymeric micelle and its degradation products. Biomacromolecules. 2001;2 (3):851–855.

[130] Liu JY, Pang Y, Huang W, et al. Redox-responsive polyphosphate nanosized assemblies: a smart drug delivery platform for cancer therapy. Biomacromolecules. 2011;12(6):2407–2415.

[131] Liu JY, Pang Y, Huang W, et al. Bioreducible micelles self-assembled from amphiphilic hyperbranched multiarm copolymer for glutathione-mediated intracellular drug delivery. Biomacromolecules. 2011;12(5):1567–1577.

[132] Jin Q, Wang Y, Cai TJ, et al. Bioinspired photo-degradable amphiphilic hyperbranched poly(amino ester)s: facile synthesis and intracellular drug delivery. Polymer. 2014;55(18):4641–4650.

[133] Bai LH, Liu XR, Yan HX, et al. Intrinsic bright green emission from hyperbranched polyphosphate esters: preparation, film fabrication and Fe^{3+} sensing. Polym Chem. 2023;14(30):3501–3511.

[134] Alexandrino EM, Ritz S, Marsico F, et al. Paclitaxel-loaded polyphosphate nanoparticles: a potential strategy for bone cancer treatment. J Mater Chem B. 2014;2 (10):1298–1306.

[135] Kretlow DJ, Mikos RG. Review: mineralization of synthetic polymer scaffolds for bone tissue engineering. Tissue Eng. 2007;13(5):927.