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Hyperbranched Poly(ester-enamine) from Spontaneous Amino-yne Click Reaction for Stabilization of Gold Nanoparticle Catalysts

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Abstract: Hyperbranched polymers have attracted much attention due to attractive properties and wide applications, such as drug controlled release, stimuli-responsive nano-objects, photosensitive materials and catalysts. Herein, Two types of novel hyperbranched poly(ester-enamine) (hb-PEEa) were designed and synthesized via the spontaneous amino-yne click reaction of A_2 monomer (1, 3-bis(4-piperidyl)-propane (A_{2a}) or piperazine (A_{2b})) and B_3 monomer (trimethylolpropanetripropiolate). According to Flory's hypothesis, gelation is an intrinsic problem in an ideal $A_2 + B_3$ polymerization system. By controlling the polymerization conditions, such as monomer concentration, molar ratio and rate of addition, a non ideal $A_2 + B_3$ polymerization system can be established to avoid gelation and to synthesize soluble hb-PEEa. Due to abundant unreacted alkynyl groups in periphery, the hb-PEEa can be further functionalized by different amino compounds or their derivates. The as-prepared amphiphilic PEG-hb-PEEa copolymer can readily self-assemble into micelles in water, which can be used as surfactant to stabilize Au nanoparticles (AuNPs) during reduction of $NaBH_4$ in aqueous solution. As a demonstration, the as-prepared PEG-hb-PEEa-supported AuNPs demonstrate good dispersion in water, solvent stability and remarkable catalytic activity for reduction of nitrobenzene compounds.

Introduction

Hyperbranched polymers (HBPs), as nano-sized highly-branched three-dimensional macromolecular architectures, have been broadly investigated and utilized in various applications including controlling drug delivery,[1-5] sensing,[6,7] and catalysis,[8-10] as well as materials science.[11-15] Because of the attractive properties and wide applications of HBPs, the development of new efficient and selective polymerizations to prepare functional HBPs is an invariably theme in polymer science. Since the concept of click chemistry was proposed in 2001, the click polymerizations had been widely utilized as a powerful technique in synthesis and modification of functional HBPs. For example, transition-metal catalyzed azide-alkyne click polymerizations (AACPs) have been widely used to synthesize hyperbranched polytriazoles.[16-21] In addition, the thiol-based click polymerizations have also been igniting great interesting in the preparation of sulfur-rich HBPs.[22-24] However, some aspects still need further enhancement in this field, i.e., the safety of azide monomers and the residue of metal catalysts in AACPs, the unpleasant smell and the limited types of thiol monomers in thiol-based click polymerizations.[25] As a result, it is challenging and very attractive to synthesize more novel functional HBPs using new click polymerizations in a mild condition.

In the past few years, Tang's group had developed several spontaneous click polymerizations including spontaneous thiol−yne click polymerization,[26] spontaneous amine−yne click polymerization,[27] and spontaneous phenol−yne click polymerization.[28] These amine−yne polymerization demonstrated obvious advantages in a catalyst-free system with high efficiency, regioselectivity, 100% atom efficiency and mild conditions. Ni et al. synthesized polymer−doxorubicin prodrug via spontaneous amino−yne click reaction.[29] The prepared polymer shows good water solubility, biocompatibility, pH response and the potential in cancer therapy. Langer et al. synthesized the water-compatible β-aminoacrylate hydrogel platforms via the click polymerization between alkynoates and secondary amines.[30] However, merely reports are relative to the synthesis of functional HBPs via this click polymerization. In the meanwhile, multi-functional HPBs can be used as templates to control the size, stability, and dispersion of metal nanoparticles (metal NPs).[31-36] For the most part, HBPs-encapsulated metal NPs are prepared by sequestering metal ions within HBPs followed by chemical reduction to yield metal NPs. The particle size of metal NPs depends on the number of metal ions initially

loaded into HBPs.[37,38] In addition, HBPs with highly branched and globular structure and multiple functional groups provide tremendous active sites and spatial constraint for aggregation of metal NPs, which are beneficial to improving efficiency in catalysis.[38-42] The terminal groups on the HBPs periphery can be tailored to control dispersion of the hybrid nanocomposites to realize homogeneous catalysis of metal nanocomposites in water or organic solvents.

Herein, Two types of novel hyperbranched poly(ester-enamine) (hb-PEEa) with regional and stereo regular structure were designed and successfully synthesized by the spontaneous amino-yne click polymerization. As a demonstration, they were utilized as surfactant to synthesis AuNPs with remarkable catalytic activity for nitrobenzene compounds. First, the A_2 + B_3 monomers polymerization strategy including the A_2-type monomer (1, 3-bis(4-piperidyl)-propane (A_{2a}) or piperazine (A_{2b})) and the B_3-type monomer (trimethylolpropanetripropiolate) was chosen to synthesize hb-PEEa. By controlling monomer concentration, molar ratio and rate of addition, the resultant hb-PEEa without gelation present good solubility in organic solvents. Abundant unreacted alkynyl groups on the periphery of hb-PEEa can be further functionalized by different amino compounds, such as n-butylamine, diethyamine and NH_2-PEG (polyethylene glycol monomethyl ether). Second, the as-prepared amphiphilic PEG-hb-PEEa synthesized through modification of NH_2-PEG containing a large number of amino and ester functions can capture gold ions and lead to the nucleation and growth of AuNPs. Therefore, PEG-hb-PEEa can be used as surfactant to synthesize AuNPs via in-situ reduction of Au ions using $NaBH_4$. The as-prepared PEG-hb-PEEa-supported AuNPs (AuNPs@PEG-hb-PEEa) show good dispersion in water and solvent stability, and remarkable catalytic activity for reduction of nitrobenzene compounds. The synthesis strategy of AuNPs@PEG-hb-PEEa provides new insight into the design and synthesis of functional metal nanocomposites.

Results and Discussion

The synthesis process and structure of AuNPs@PEG-hb-PEEa are schematically shown in **Figure 1**. The hb-PEEa is synthesized via the spontaneous amino-yne click polymerization of A_2 monomer (1,3-bis(4-piperidyl)-propane (A_{2a}) or piperazine (A_{2b})) and B_3 monomer (trimethylolpropanetripropiolate), which

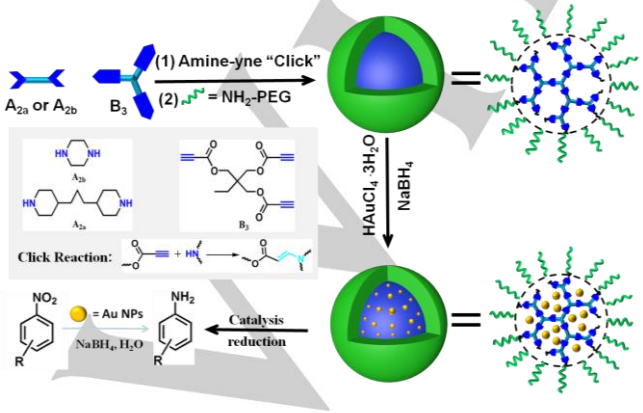

Figure 1. Schematic synthesis process and structure of AuNPs@PEG-hb-PEEa and application in catalytic reduction of nitrobenzene compounds.

can be further functionalized by NH_2-PEG. The structure of B_3 monomer was characterized by FT-IR and NMR spectroscopy (**Figure S1**). The as-prepared amphiphilic PEG-hb-PEEa can effectively stabilize AuNPs. The resultant AuNPs@PEG-hb-PEEa composites efficiently catalyze reduction of nitrobenzene compounds in the presence of $NaBH_4$.

In this study, the A_2 + B_3 monomers polymerization strategy is applied to the synthesis of HBPs. According to Flory's hypothesis, gelation is an intrinsic problem in an ideal A_2 + B_3 polymerization system.[43-46] During the polymerization of A_2 with B_3 monomers, the gelated products take place when monomer solids are directly added or the addition of monomer solution is too quick. Besides the monomer concentration, other factors, such as slow addition of one monomer to another, monomer molar ratio, also account for avoiding gelation. Because of the high activity and efficiency of the amino-yne click reaction, the total monomer concentration should be lower and higher monomer concentration leads to insoluble products. Through slow addition approach to avoid any high local concentration, fully soluble hb-PEEa-1 (Entry 2-5, **Table 1**) could be synthesized by polymerization of A_{2a} and B_3 monomers at different molar ratios. As increasing the molar ratio of B_3 monomer, the average molecular weight (M_n and M_w) and polydispersity index (PDI) decreased accordingly. hb-PEEa-1 (Entry 5) with M_n = 8940 g mol^{-1} and PDI = 2.88 was synthesized at the molar ratio of 1.0/1.2. On the contrary, severe gelation quickly occurred at A_{2a}/B_3 molar ratio of 1.5/1.0 (equal molar concentration of functional groups) under the same polymerization conditions (Entry 1). Furthermore, hb-PEEa-2 (Entry 6) with M_n = 5080 g mol^{-1} and PDI = 3.02 was obtained via the polymerization of A_{2b} and B_3 monomer at the molar ratio of 1.0/1.2. Therefore, by controlling the polymerization conditions, a non ideal A_2 + B_3 polymerization system was established to avoid gelation and to synthesize soluble hb-PEEa via the spontaneous amino-yne click reaction. The synthesis strategy of hb-PEEa provides a helpful reference for the design and synthesis of HBPs via A_2 + B_3 monomers polymerization.

Table 1. Polymerization condition for hyperbranched poly(ester-enamine) via spontaneous amino-yne click reaction.

Entry[a]	A_2 : B_3 (molar ratio)	M_w[b] [g mol^{-1}]	M_n[b] [g mol^{-1}]	PDI[b]
1[c]	A_{2a} : B_3 = 1.5 : 1.0	insoluble	insoluble	insoluble
2[d]	A_{2a} : B_3 = 1.0 : 1.0	36,270	6,990	5.19
3	A_{2a} : B_3 = 1.0 : 1.0	197,610	33,280	5.94
4	A_{2a} : B_3 = 1.0 : 1.1	80,580	25,550	3.16
5	A_{2a} : B_3 = 1.0 : 1.2	25,780	8,940	2.88
6	A_{2b} : B_3 = 1.0 : 1.2	15,360	5,080	3.02

[a] Carried out in THF under nitrogen for 24 h; monomer concentration (A_2 = 20 mM); all yields over 90% by precipitation from hexane. [b] Molecular weight (g mol^{-1}) determined by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration: M_w = weight-average molecular weight, M_n = number-average molecular weight, PDI = M_w/M_n. [c] Molecular weight could not be obtained because the polymer was not soluble in common solvents. [d] Reaction time is for 12 h.

By optimizing the polymerization conditions, hb-PEEa can be rapidly and effectively synthesized. The resultant hb-PEEa is soluble in common organic solvents such as dichloromethane, acetone, ethanol, and tetrahydrofuran. The molecular structure

of hb-PEEa was identified by FT-IR and NMR spectroscopy. By analyzing the FT-IR spectra of A_{2a} monomer, B_3 monomer, and hb-PEEa-1 (**Figure S2a**), the N−H vibration of A_{2a} monomer occurs at 3190.0 cm^{-1}, which disappears completely after polymerization. The characteristic absorptions of B_3 monomer at 3242.2 and 2119.7 cm^{-1} can be assigned to the ≡C-H and C≡C stretching vibrations, which weak in the hb-PEEa-1. The key absorption of new C=C is at 1609.1 cm^{-1} in the hb-PEEa-1. These results reveal the occurrence of the polymerization and there are many unreacted alkynyl groups in its periphery. From the ^{1}H NMR spectrum (**Figure 2a**), two new peaks (**l** and **m**) assigned to the resonances of the vinylene protons appear at 7.4 and 4.6 ppm in the spectra of hb-PEEa-1. The ≡C-H (**n**) of B_3 monomer at 2.9 ppm was shifted to 4.21 ppm in hb-PEEa-1. And the intensity of the alkynyl units becomes weaker after polymerization, which also indicates alkynyl units as terminal units. Furthermore, the hb-PEEa-1 was investigated by ^{13}C NMR spectroscopy (**Figure S3**). There are some characteristic signals at 169.8, 152.7, 151.2 and 83.4 ppm, which represent the carbon atoms of the ester carbonyl units and the vinylene groups, respectively. The molecular structure of hb-PEEa-2 was also characterised by FT-IR (**Figure S2b**) and NMR (**Figure 2b** and **S4**). The analysis results show that hb-PEEa-2 can be successfully synthesized by the amino-yne click reaction of A_2 and B_3 monomers.

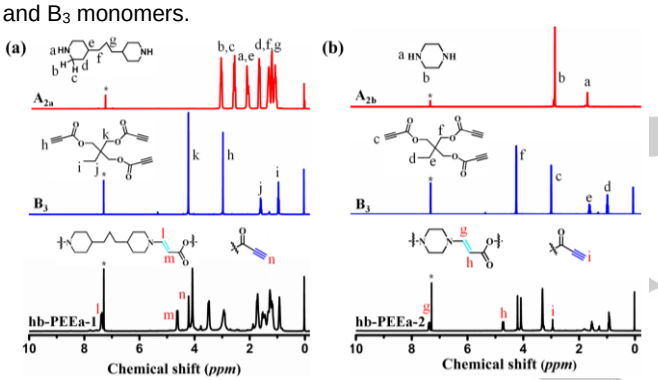

Figure 2. ^{1}H NMR spectra in $CDCl_3$: (a) A_{2a}, B_3 and hb-PEEa-1; (b) A_{2b}, B_3 and hb-PEEa-2.

According to structure analysis of hb-PEEa, there are a large number of unreacted alkynyl groups in the periphery of hb-PEEa, which can be further functionalized via spontaneous amino-yne reaction. By simply mixing the hb-PEEa and the different amines such as n-butylamine, diethyamine and NH_2-PEG (polyethylene glycolmonomethyl ether, M_n = 2000 g mol^{-1}) in THF at room temperature for 12 h, the quantitative reaction of the terminal alkynyl groups was observed by FT-IR and ^{1}H NMR spectroscopy. The vibration of ≡C−H completely disappears and the absorption of C=C enhances after post-polymerization in the FT-IR spectrum (**Figure S5**). By analyzing the ^{1}H NMR spectra (**Figure S6** and **S7**), we can observe some peaks of new vinylene protons with the disappearance of the alkynyl groups. As indicated by the GPC measurement, the M_n of PEG-hb-PEEa-1 (78670 g mol^{-1}) and PEG-hb-PEEa-2 (30430 g mol^{-1}) are enhanced compared with that of hb-PEEa-1 (8940 g mol^{-1}) and hb-PEEa-2 (5080 g mol^{-1}), respectively, Meanwhile, the PEG-modified hb-PEEa (PEG-hb-PEEa) is soluble in water in contrast to hb-PEEa.

The amphiphilic PEG-hb-PEEa contains a large number of amino and ester functions, which can be used to capture metal ions, guide the nucleation and growth of metal NPs, and enhance the non-covalent interaction between support and loaded metal NPs. Therefore, PEG-hb-PEEa can be used as organic templates to stabilize AuNPs in water. AuNPs@PEG-hb-PEEa is synthesized by mixing PEG-hb-PEEa and $HAuCl_4$•$3H_2O$ in deionized water under vigorous stirring. During the process, Au(III) ions are sequestered into PEG-hb-PEEa. A freshly prepared $NaBH_4$ solution is then added dropwise into the as-prepared solution. Then Au (III) ions are reduced by $NaBH_4$, and the Au(0) atoms gather together to form stable AuNPs inside the PEG-hb-PEEa. The color of the solution gradually becomes purple with the formation of AuNPs. The size and morphology of AuNPs are determined by typical transmission electron microscope (TEM) (**Figure 3a** and **3b**). The DLS analysis displays the hydrodynamic behavior, and AuNPs@PEG-hb-PEEa has a narrow dispersion in aqueous solution by the DLS measurement (**Figure 3c**). Moreover, UV−vis spectra reveal the plasmonic properties of AuNPs, with the change of the surface plasmon band (SPB) along with the variety of sizes. The surface plasmon band (SPB) is observed at 531 nm for AuNPs@PEG-hb-PEEa-1, 524 nm for AuNPs@PEG-hb-PEEa-2 (**Figure 3d**). Furthermore, we found that the micelle size and color in aqueous solution do not change under environmental conditions for several weeks, which indicated AuNPs@PEG-hb-PEEa has good solvent stability. The final content of gold is 1.2 wt% (AuNPs@PEG-hb-PEEa-1) and 1.8 wt% (AuNPs@PEG-hb-PEEa-2) from ICP analysis, respectively. In a word, the as-prepared amphiphilic PEG-hb-PEEa copolymer can readily self-assemble into micelles in water. And the heteroatom-rich PEG-hb-PEEa also provides an extra support for the formation and stabilization of Au NPs through its non-covalent interaction with Au ions or NPs. These advantages are beneficial to the synthesis of metal nanocomposites. AuNPs@PEG-hb-PEEa can be synthesized via infiltration of $HAuCl_4$•$3H_2O$ and in situ reduction using $NaBH_4$. AuNPs@PEG-hb-PEEa with good dispersion in water and solvent stability suggests promising applications in aqueous media.

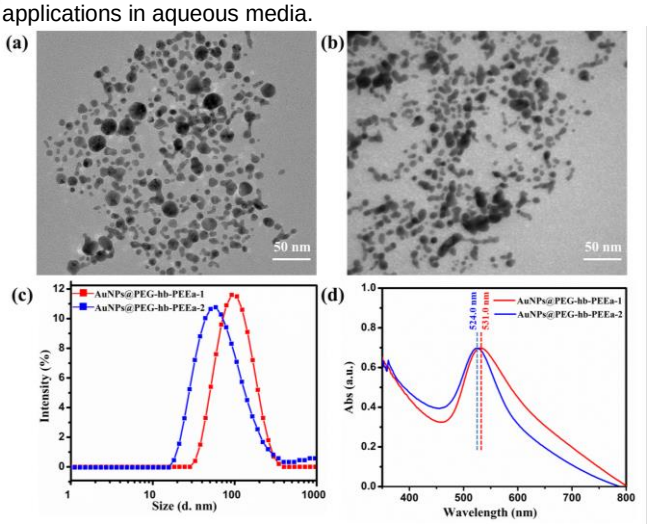

Figure 3. TEM images of Au NPs: (a) AuNPs@PEG-hb-PEEa-1 and (b) AuNPs@PEG-hb-PEEa-2; (c) DLS size distribution; (d) UV-vis spectra.

Nitrobenzene compounds are toxic and hazardous pollutants in industrial and agricultural waste water. They have high stability and low solubility in water, so their degradation in nature has always been difficult and challenging.[47,48] In general, *p*-nitrophenol (4-NP) reduction in the presence of $NaBH_4$ is a versatile reaction to evaluate the catalytic activity of various metal NPs, and this reaction can also be readily monitored by UV−vis spectroscopy. The as-prepared AuNPs@PEG-hb-PEEa has good dispersion in water and solvent stability, and its application in catalysis was explored. The reduction of 4-NP in the excess presence of NaBH4 was chosen as a model reaction to evaluate the catalytic activity of AuNPs@PEG-hb-PEEa and monitored dynamically by UV-Vis spectra. As a control experiment, the reaction did not occur when using only PEG-hb-PEEa as catalyst. The intensity of the absorption peak at 400 nm, a characteristic peak of 4-NP and $NaBH_4$, remains almost unchanged in the presence of PEG-hb-PEEa at a prolonged period. This means that the PEG-hb-PEEa alone does not have catalytic activity. By adding AuNPs@PEG-hb-PEEa as a catalyst, the reduction was initiated immediately, showing the rapid decrease of the absorption at 400 nm and the related increase of the characteristic peak of p-aminophenol (**Figure 4a** and **4b**). And the color of the solution gradually changed from bright yellow to colorless (**Figure 4c**, inset image). Since $NaBH_4$ was used in excess compared to the 4-NP in the system, the reduction of 4-NP can be considered as a pseudo-first order reaction to evaluate the kinetic reaction rate of the catalytic reaction. Herein, **Figure 4d** show a linear correlation of ln(At/A0) versus time at any instant. K_{app} (the apparent rate constant) is 12.80×10^{-3} s^{-1} for AuNPs@PEG-hb-PEEa-1 and 21.78×10^{-3} s^{-1} for AuNPs@PEG-hb-PEEa-2. In order to ensure the universal applicability of AuNPs@PEG-hb-PEEa, other nitrobenzene compounds with different substituent groups were also considered (**Figure S8**). The results illustrate that the AuNPs@PEG-hb-PEEa exhibit efficient catalytic activity for the reduction of other nitrobenzene compounds. The substituent has a great influence on the rate of reduction reaction, and the electron withdrawing groups (Br or F) have a faster reaction, compared with the electron donating groups.[49] These results show that AuNPs@PEG-hb-PEEa exhibits remarkable catalytic activity toward the reduction of a series of nitrobenzene compounds. The synthesis and application of AuNPs@PEG-hb-PEEa provide great opportunities to prepare functional metal nanocatalysts with potential in the homogeneous catalysis field.

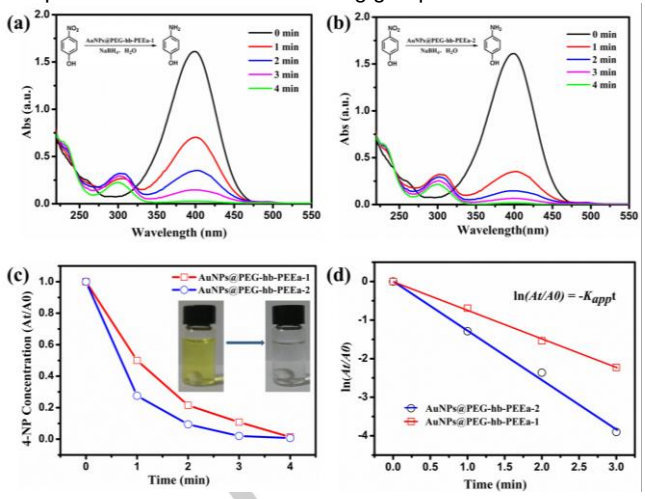

Figure 4. Time-dependent UV-vis spectra of the reduction of p-nitrophenol (0.9 μmol) and 0.09 mmol NaBH4 catalyzed by 60 μL AuNPs@PEG-hb-PEEa solution (1 mg/mL), (a) AuNPs@PEG-hb-PEEa-1 solution; (b) AuNPs@PEG-hb-PEEa-2 solution; (c) At/A0 as a function of reaction time, Inset images: typical optical images of reaction mixtures at 0 and 4 min; (d) linear relationship of ln(At/A0) as a function of time.

Conclusion

In summary, Two types of novel hyperbranched poly(ester-enamine) were successfully synthesized via the spontaneous amino-yne click polymerization of A_2 monomer (1,3-bis(4-piperidyl)-propane (A_{2a}) or piperazine (A_{2b})) and B_3 monomer (trimethylolpropanetripropiolate). By optimizing the polymerization conditions, gelation can be successfully avoided and the resultant hb-PEEa shows good solubility in common organic solvents. The hb-PEEa can be further functionalized via amine−yne click reactions. PEG-modified hb-PEEa (PEG-hb-PEEa) can readily self-assemble into micelles in water, which can be used as surfactant to stabilize AuNPs. The as-prepared AuNPs@PEG-hb-PEEa shows good catalytic activity for efficient reduction of nitrobenzene compounds under mild conditions.

Experimental Section

Materials

All reagents and solvents were purchased from J.&K. Scientific Ltd (Beijing, China). Tetrahydrofuran (THF) was distilled through sodium under dry nitrogen before using. Other solvents were used without further purification. Reactions were followed with TLC (0.254 mm silica gel 60-F plates). Flash chromatography was carried out on silica gel of 200–300 mesh.

Synthesis of trimethylolpropanetripropiolate (B_3 monomer). Trimethylolpropane (40.25 g, 0.30 mol) and Propiolic acid (70.05 g, 1.0 mol) were added to the benzene (250 mL) with 5 mol% P-toluenesulfonic acid used as catalyst. A Dean-stark trap and a condenser were attached, and the reaction was protected under nitrogen. The mixture was heated to reflux for 24 h. Then the mixture was allowed to reach room temperature and diluted with EtOAc (250 mL), washed with 5 wt% Na_2CO_3 aqueous solution and brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the purification of the reaction mixture by silica gel column chromatography eluting with EtOAc/petroleum (1/3) was performed to afford the product. IR (KBr, *v*, cm^{-1}): 3292.34, 3242.19, 2985.67, 2119.67, 1718.50, 1217.03, 983.65, 756.06, 707.84. ^1H NMR (400 MHz, $CDCl_3$) δ 4.19 (s, 6H), 2.93 (s, 3H), 1.56 (t, *J* = 8.0 Hz, 2H), 0.92 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 75.9, 74.2, 66.3, 40.8, 22.9, 7.4.

Synthesis of hyperbranched poly(ester-enamine) (hb-PEEa). The polymerization of A_{2a} and B_3 monomers at the molar ratio of 1/1.2 is given below as an example. A single-necked 25 mL flask equipped with a magnetic stir bar was added 1, 3-bis(4-piperidyl)-propane (A_{2a} momomer) (42 mg, 0.2 mmol) and tetrahydrofuran (THF, 4 mL). Trimethylolpropanetripropiolate (B_3 monomer) (70 mg, 0.24 mmol) in 4 mL THF was injected into the above solution by syringe over 0.5 h. The mixture was stirred under dry nitrogen for 24 h at room temperature, and then the solution was poured slowly into an excess amount of hexane. The precipitate was collected and dried at room temperature under vacuum.

Characterization data for hb-PEEa-1 synthesized through the polymerization A_{2a} and B_3 monomers. IR (KBr, *v*, cm^{-1}): 2926.67, 2845.77, 2117.78, 1688.44, 1609.11, 1455.11, 1237.33, 1123.77. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (d, 1H), 4.64-4.61 (d, 1H), 4.21 (s,

0.8H), 4.08 (s, 2.1H), 3.50-3.47 (m, 2.1H), 2.94-2.91 (m, 2.4H), 1.71 (s, 2.8H), 1.54-1.17(m, 7.6H), 0.92 (s, 1.7H).

Characterization data for hb-PEEa-2 synthesized through the polymerization A_{2b} and B_3 monomers. IR (KBr, ν, cm^{-1}): 3253.33, 2968.67, 2113.11, 1697.78, 1602.89, 1448.89, 1349.33, 1224.89, 1142.44, 1004.00. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.29 (m, 1.0H), 4.73 (d, 1.0H), 4.21 (s, 1.4H), 4.09 (s, 2.0H), 3.31 (s, 4.0H), 2.95-2.92 (m, 0.7H), 1.80 (s, 0.6H), 1.58-1.51 (m, 1.1H), 1.28 (s, 0.5H), 0.95-0.88 (m, 2.0H).

Modification of hb-PEEa by amino-yne reaction. A solution of amine compound (n-butylamine (7.3 mg) or diethyamine (7.3 mg) or NH_2-PEG (polyethylene glycolmonomethyl ether, M_n = 2000 g mol^{-1}, 200 mg) in 2 mL THF was added dropwise to a solution of hb-PEEa-1 (50 mg, M_n = 8940 g mol^{-1}, PDI = 2.88) or hb-PEEa-2 (38 mg, M_n = 5080 g mol^{-1}, PDI = 3.02) in THF (4 mL). The mixture was stirred under dry nitrogen at room temperature for 12 h, and then added dropwise into hexane. The precipitate was collected by filtration and dried at room temperature under vacuum.

Preparation of AuNPs@ PEG-hb-PEEa. AuNPs@PEG-hb-PEEa was synthesized by mixing PEG-hb-PEEa-1 (10 mg, M_n = 78670 g mol^{-1}) or PEG-hb-PEEa-2 (10 mg, M_n = 30430 g mol^{-1}) and $HAuCl_4 \cdot 3H_2O$ (3 mg, 0.008 mmol) in deionized water (10 mL) under vigorous stirring for 1h. Then a freshly-prepared $NaBH_4$ (40 mg in 2 mL water) aqueous solution was added dropwise into the as-prepared solution. The obtained solution was continuously stirred for another 2 h. The AuNPs@PEG-hb-PEEa was purified by dialysis against a large volume of water (3 × 100 mL). The AuNPs@PEG-hb-PEEa was collected by freeze-drying.

Characterization

All NMR spectra were obtained at ambient temperature using a Bruker-400 MHz spectrometer. Chemical shifts (δ) were reported as part per million (ppm) on the δ scale downfield from TMS. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet. Fourier transform infrared spectroscopy (FT-IR) measurement was conducted on an FT-IR spectrophotometer (PerkinElmer, USA). Transmission electron microscopy (TEM, FEI, Tecnai G2 F20) was performed at 200 kV. Samples for analysis were dispersed in alcohol and deposited on a holey carbon/Cu grid (200 mesh). UV-vis spectra were recorded using a spectrophotometer UV-2550 model (Shimadzu, Japan). Dynamic light scattering (DLS) measurements were made with a Zetasizer Nano-ZS (Malvern Instruments, UK). The samples were filtered using a microfilter (0.45 μm) prior to measurement. The number-average and weight-average molecular weight (M_n and M_w, respectively) and polydispersity index (PDI = M_w/M_n) were determined by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration. Gel permeation chromatography (GPC) measurements were conducted using a system equipped with a Waters 515 pump, a Waters UV-vis detector and a column temperature controller with a flow rate of 1.0 mL min−1 in THF (HPLC grade) at 25 °C.

Reduction of nitrobenzene compounds catalyzed by AuNPs@ PEG-hb-PEEa. The catalytic activity of AuNPs@PEG-hb-PEEa was examined by the reduction of nitrobenzene compounds in the presence of $NaBH_4$. In a typical experiment, an aqueous solution (3 mL) containing 0.9 μmol of p-nitrophenol and 0.09 mmol of $NaBH_4$ were added in a quartz cuvette. Then AuNPs@PEG-hb-PEEa catalyst in water (60 μl, 1 mg/mL) was introduced, and the reaction progress was detected by UV−vis spectroscopy. And the initial bright yellow solution gradually turned to colorless as the reaction progressed.

Supporting Information

Supporting Information is available from the Online Library or from the author.

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Conflict of interest

The authors declare no competing financial interest.

Keywords: hyperbranched polymers • amino-yne click reaction • nanocatalyst • reduction reaction

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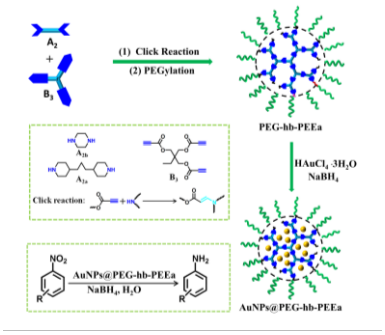

Novel hyperbranched poly(ester-enamine) (hb-PEEa) was synthesized by the spontaneous amino-yne click reaction of A_2 + B_3 monomers. The amphiphilic PEG-hb-PEEa was used as surfactant for stabilization of Au nanoparticles (AuNPs). The PEG-hb-PEEa-supported AuNPs nanocomposites (AuNPs@PEG-hb-PEEa) showed remarkable catalytic activity for catalytic reduction of nitrobenzene compounds.