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Synthesis of Conjugated Hyperbranched Polytriazoles Containing Truxene Units by Click Polymerization

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It has been a challenge to synthesize high molecular weight and soluble conjugated hyperbranched poly(1,2,3-triazole)s (hb-PTAs). In this paper a series of soluble hyperbranched polytriazoles, whose number-average molecular weight (M_n) and polydispersity index ranged in (1.2—3.3)×10^4 and 1.7—3.0, respectively, were synthesized with A_2+B_3 approach. In the polymerization process, diazides **A1**—**A4** and triyne **B1** were used as A_2 and B_3 monomers; Cu(I)-catalyst, THF and water were used as their reaction system. At room temperature the final molecular weight could be controlled through reaction time, so finally we obtained soluble conjugated hyperbranched poly(1,2,3-triazole)s hb-PTAs (**1**—**4**). The polymers were soluble in common organic solvents, and all emitted blue light; the films of polymers emitted yellow and blue light, due to the difference in the aggregation of their chromophoric units in the solid state. The thermal properties of the final copolymers were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Keywords "click" polymerization, hyperbranched, aggregation

Introduction

Because of its remarkable features such as nearly quantitative yields, mild reaction conditions, broad tolerance toward functional groups, low susceptibility to side reactions, and simple product isolation, the "click reaction" has been attempted to develop into a new polymerization technique.[1-16] A "click reaction" can create functional molecules with heteroatom links from reactive modular building blocks in high efficiency under benign conditions through simple isolation procedures.[17-20] A number of click reactions have been explored and identified, especially, the copper Cu(I)-catalyzed Huisgen cycloaddition, also termed as the Sharpless "click" reaction, that is the typical example and has been successfully applied to macromolecular chemistry.[21-33]

Various polymeric materials including block copolymers, dendrimers, and complex macromolecular structure are synthesized using the "click reaction",[34-50] however the conjugated hyperbranced polymers synthesized by the "click reaction" are still scarcely reported, because the Cu(I)-catalyzed polymerizations of arylenediazides (N_3-Ar-N_3) and arylenediynes (HC≡C-Ar-C≡CH) (Ar＝phenyl, pyridyl, fluorenyl, *etc*.) were sluggish, taking as long as 7—10 d to finish, and usually the production precipitated from the reaction mixtures.[19,21,53] Two AB_2-type monomers of azidoarylenediynes with a general formula of N_3-Ar-$(C{\equiv}CH)_2$ prepared by two groups in Germany and Belgium failed to be converted into soluble polymer,[54,55] A_2+B_3 type monomers are reported by Tang groups, which also failed to form soluble polymer using the copper Cu(I)-catalyzed systems.[19] Recently, Li and Tang *et al*. have reported the synthesis of the soluble hypebranched polytriazoles.[56-58] The poor activity or low solubility of the phen-monomers, which one has more influence on the polymerization under the copper Cu(I)-catalysis? So we brought out a series of reactions to find the best polymerization condition.

Hyperbranched polymer can be obtained by the self-condensation of AB_n monomers,[48] but there are some limitations such as tedious synthesis for asymmetric functionality and self-oligomerization during storage. The A_2+B_3 type of polymerization has been demonstrated to be a facile method to achieve hyperbranched polymers, as the monomers are easily obtained and free of the self-oligomerization problem encountered in the AB_n system. In our work , we took the A_2+B_3 type of polymerization to synthesize a series of conjugated hyperbranched polymer hb-PTAs (**1**—**4**) (hb-PTAs1,

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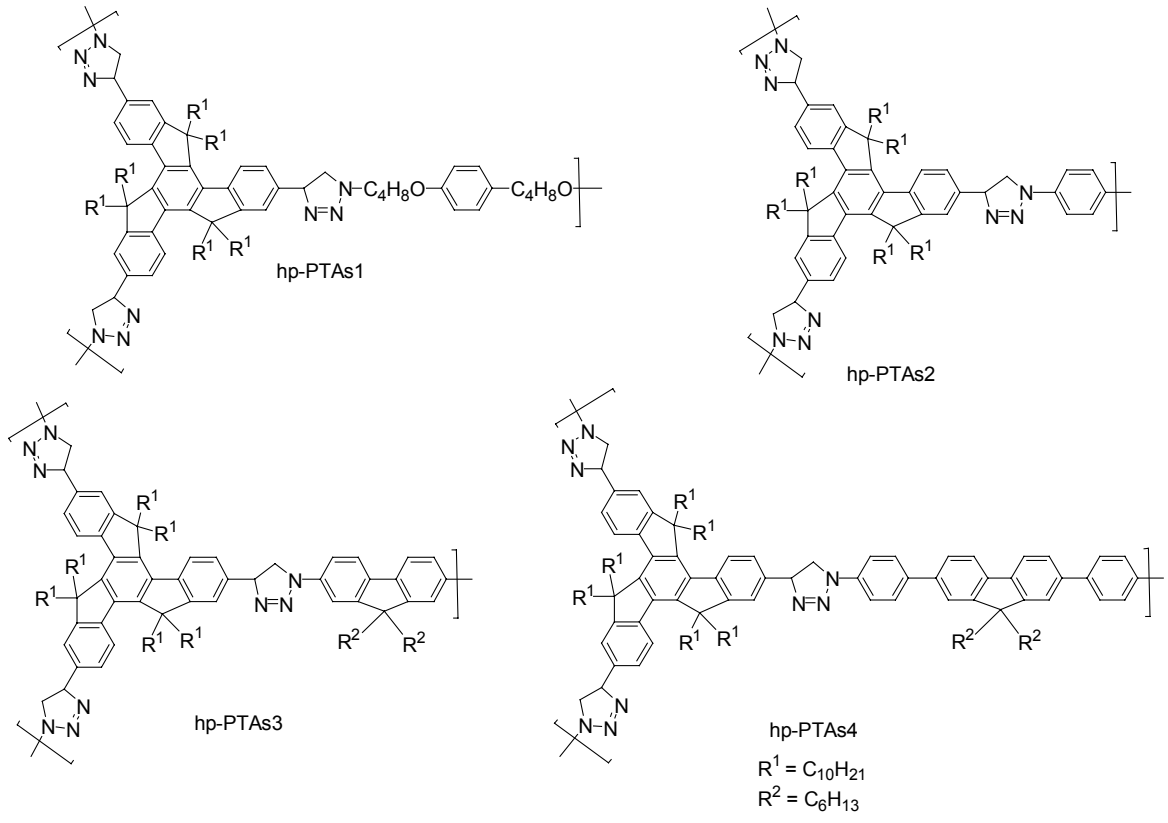
hb-PTAs2, hb-PTAs3 and hb-PTAs4) (Scheme 1), the polymers were soluble in common organic solvents, and the number-average molecular weight (M_n) and polydispersity index ranged in (1.2—3.3)×10^4 and 1.7—3.0, respectively. The A_2 monomers **A1**—**A4** easily react with the B_3 monomer (**B1**) in THF/H_2O and Cu(I)-catalyzed system, moreover, the polymers will precipitate from the solution if the reaction time is too long. The precipitation of hb-PTAs1 and hb-PTAs2 is difficultly dissolved, otherwise the precipitation of hb-PTAs3 and hb-PTAs4 is easily soluble in common solution. The soluble Polymers of hb-PTAs1 and hb-PTAs2 can be obtained by controlling reaction time. Finally we synthesized soluble conjugated hyperbranched polymer by click polymerization. All the polymer emitted blue light in solution; and the films of polymers emitted yellow and blue light due to the difference in the aggregation.

Experimental

Materials and instruments

All chemicals were purchased from Aldrich or Acros and used without further purification. 9,9-Dihexylfluorene, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxa-borolan-2-yl)-9,9-dihexylfluorene,[59] *N*-(*t*-butoxycarbonyl)-1-amino-4-bromobenzene,[60] the A_2-type monomer of diazides A1,[19] and 2,7,12-triiododecaethyltruxene[61] were prepared according to literature procedures. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature.[53] All solvents were purified and dried by standard methods. The reactions were monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200—300 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV600 spectrometer in $CDCl_3$. The gel permeation chromatography (GPC) measurements were performed on a Waters 410 system using polystyrene standards with THF as an eluent at 30 ℃, a set of one column of PL gel MIX-C (500—3×10^6) was equipped. Electronic absorption spectra were obtained on a SHIMADZU UV-visible spectrometer model UV-2500. Fluorescence spectra were recorded on a SHIMADZU RF-5301PC. Elemental analyses were performed on a Flash EA 1112 analyzer. The thermal gravimetric analysis (TGA) (Pyris 1 TGA) and differential scanning calorimetry (DSC) (TA 2910) measurements were carried out under a nitrogen atmosphere at a heating rate of 10 ℃/min. The matrix assisted laser desorption ionization time of flight (MALDI-TOF) MS spectrometric measurements were performed on a Bruker BIFLEXIII mass spectrometer.

Scheme 1 Structure of hypbranched polymers hb-PTAs (**1**—**4**)



General procedure for the synthesis of monomers A1—A4 from the amine precursor

The amine precursor monomers were dissolved in 2% aqueous hydrochloric acid, cooled to 0 ℃, then $NaNO_2$ was added. The mixture was stirred for 1 h at 0 ℃, NaN_3 was added and stirred for 4 h at 0 ℃. Water and CH_2Cl_2 (50 mL) were added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 twice, and the combined organic layers were dried over Na_2SO_4. After removal of the solvent, the crude product was chromatographically purified on silica gel eluting with hexane to afford **A1**—**A4**.

Synthesis of monomer A2

1,4-Diaminebenzene (1.00 g, 9.2 mmol), $NaNO_2$ (1.50 g, 21.7 mmol) and NaN_3 (1.50 g, 23 mmol) were used, **A2** was obtained as brown solid (1.40 g, 94%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.06 (s, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 136.7, 120.4. Anal. calcd for $C_6H_4N_6$: C 45.00, H 2.52, N 52.48; found C 45.05, H 2.50, N 52.42.

Synthesis of 2,7-dinitro-9,9-dihexylfluorene (1)

A mixture of 9,9-dihexylfluorene (1.00 g, 3.0 mmol), acetic acid (80 mL), condensed sulfuric acid (10 mL) and condensed nitric acid (2 mL) was stirred for 12 h at 95 ℃, then cooled to room temperature and the yellow precipitation was filtered. The crude product was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane (1∶3, *V*/*V*) to afford 2,7-dinitro-9,9-dihexylfluorene (**1**) as a yellow solid (1.10 g, 82%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.33 (d, J=8.4 Hz, 2H), 8.26 (s, 2H), 7.92 (d, J=8.4 Hz, 2H), 2.12—2.09 (m, 4H), 1.12—1.08 (m, 8H), 1.03—0.97 (m, 4H), 0.76 (t, J=7.2 Hz, 6H), 0.57—0.54 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 153.5, 148.5, 144.7, 123.2, 121.6, 118.5, 56.5, 39.8, 31.4, 29.4, 23.8, 22.5, 13.9. Anal. calcd for $C_{25}H_{32}N_2O_4$: C 70.73, H 7.60, N 6.60; found C 70.60, H 7.44, N 6.43.

Synthesis of 2,7-diamine-9,9-dihexylfluorene (2)

A mixture of 2,7-dinitro-9,9-dihexylfluorene (0.50 g, 1.2 mmol), zinc powder (2.00 g), anhydrous $CaCl_2$ (0.30 g), alcohol (30 mL) and water (10 mL) was refluxed for 5 h, and the hot mixture was filtered to remove the zinc powder. Water and CH_2Cl_2 (50 mL) were added, then the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (×2), and the combined organic layers were dried over Na_2SO_4. After removal of the solvent, the crude product was chromatographically purified on silica gel eluting with ethyl acetate/hexane (1∶3, *V*/*V*) to afford 2,7-diamine-9,9-dihexylfluorene (**2**) (0.45 g, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.34 (d, J=7.7 Hz, 2H), 6.62 (d, J=7.7 Hz, 4H), 3.52 (br s, 4H), 1.84 (t, J=8.2 Hz, 4H), 1.17—1.13 (m, 4H), 1.10—1.03 (m, 8H), 0.78 (t, J=7.1 Hz, 6H), 0.69—0.64 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.4, 151.2, 144.0, 126.5, 118.4, 109.6, 54.2, 40.4, 31.1, 29.4, 23.1, 13.6. MALDI-TOF *m*/*z*: calcd 364, found 364.

Synthesis of 2,7-diazide-9,9-dihexylfluorene (A3)

2,7-Diamine-9,9-dihexylfluorene (0.40 g, 1.1 mmol), $NaNO_2$ (0.18 g, 2.3 mmol) and NaN_3 (0.16 g, 2.5 mmol) were used, **A3** was obtained as yellow solid (0.42 g, 92%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.60 (d, J=8.4 Hz, 2H), 7.00 (d, J=8.4 Hz, 2H), 6.94 (s, 2H), 1.92 (t, J=8.4 Hz, 4H), 1.13—1.10 (m, 4H), 1.08—1.03 (m, 8H), 0.77 (t, J=7.2 Hz, 6H), 0.59—0.55 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 152.6, 138.8, 137.6, 120.5, 117.9, 113.6, 55.5, 40.4, 31.5, 29.6, 23.6, 22.6, 14.0. Anal. calcd for $C_{25}H_{32}N_6$: C 72.08, H 7.74, N 20.17; found C 72.02, H 7.47, N 19.30.

Synthesis of compound 3

A mixture of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (0.15 g, 0.26 mmol), *N*-(*t*-butoxycarbonyl)-1-amino-4-bromobenzene (0.15 g, 0.55 mmol), $NaHCO_3$ (0.50 g, 5.6 mmol), H_2O (5 mL), and THF (25 mL) was carefully degassed before $Pd(PPh_3)_4$ (8 mg, 0.08 mmol) was added. The mixture was refluxed for 24 h under stirring. Water and CH_2Cl_2 (50 mL) were added, then the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (×2), and the combined organic layers were dried over Na_2SO_4. After removal of the solvent, the crude product was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane (1∶1, *V*/*V*) to afford compound **3** as a white solid (0.15 g, 81%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.73 (d, J=7.8 Hz, 2H), 7.60 (d, J=8.4 Hz, 4H), 7.54 (d, J=7.8 Hz, 2H), 7.52 (s, 2H), 7.46 (d, J=8.4 Hz, 4H), 6.57 (s, 2H), 2.05—2.00 (m, 4H), 1.55 (s, 18H), 1.12—1.03 (m, 12H), 0.76—0.71 (m, 10H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 152.7, 151.7, 139.8, 139.4, 137.6, 136.5, 127.7, 125.7, 121.1, 119.9, 118.8, 55.2, 40.4, 31.5, 29.7, 28.3, 23.8, 22.6, 14.0. Anal. calcd for $C_{47}H_{60}N_2$: C 78.73, H 8.43, N 3.91; found C 78.63, H 8.47, N 3.80.

Synthesis of monomer A4

A mixture of compound **3** (0.12 g, 0.17 mmol), ether (30 mL) and condensed aqueous hydrochloric acid (20 mL) was stirred for 24 h at room temperature. After removal of the ether, 2% aqueous hydrochloric acid (20 mL) was added. $NaNO_2$ (0.025 g, 0.36 mmol) was added and the mixture was stirred for 1 h at 0 ℃, then NaN_3 (0.035 g, 0.54 mmol) was added and stirred for 12 h under 4 ℃. Water and CH_2Cl_2 (50 mL) were added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (×2), and the combined organic layers were dried over Na_2SO_4. After removal of the solvent, the crude product was chromatographically purified on silica gel eluting with hexane to afford compound **A4** as a yellow solid (0.076 g, 80%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.76 (d, J=7.8 Hz, 2H), 7.66 (d, J=8.4 Hz, 4H), 7.55 (d, J=7.8 Hz, 2H), 7.53 (s, 2H), 7.13 (d, J=8.4 Hz, 4H), 2.05—2.01 (m, 4H), 1.12—

1.04 (m, 12H), 0.76—0.70 (m, 10H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 151.8, 140.1, 139.1, 139.0, 138.5, 128.5, 125.8, 121.2, 120.1, 119.9, 55.3, 40.4, 31.5, 29.7, 23.8, 22.5, 14.0. Anal. calcd for $C_{37}H_{40}N_6$: C 78.14, H 7.09, N 14.78; found C 78.09, H 7.13, N 14.83.

Synthesis of 2,7,12-trimethylsilicaethynyl-decaethyltruxene (compound 4)

A mixture of 2,7,12-triiododecaethyltruxene (2.10 g, 1.5 mmol), trimethylsilicaethyne (3 mmol), THF (25 mL) and diisopropylamine (13 mL) was carefully degassed before $Pd(PPh_3)_2Cl_2$ (0.12 g, 0.17 mmol) was added. The mixture was refluxed for 24 h under nitrogen, vacuumed to dryness, and the crude product was chromatographically purified on silica gel eluting with hexane to afford compound **4** as a slightly yellow solid (1.97 g, 90%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.26 (d, J=7.8 Hz, 3H), 7.53 (s, 3H), 7.51 (d, J=7.8 Hz, 3H), 2.87—2.83 (m, 6H), 2.07—2.02 (m, 6H), 1.19—1.14 (m, 12H), 1.12—1.07 (m, 12H), 1.06—1.02 (m, 12H), 1.00—0.96 (m, 12H), 0.90—0.87 (m, 18H), 0.83—0.80 (m, 36H), 0.47—0.40 (m, 12H), 0.31 (s, 27H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 153.5, 146.0, 140.5, 137.9, 130.4, 125.5, 124.3, 120.9, 105.9, 94.4, 55.7, 36.8, 29.8, 29.6, 29.4, 29.3, 23.9, 22.6, 14.1. Anal. calcd for $C_{102}H_{162}Si_3$: C 83.19, H 11.09; found C 83.22, H 11.15.

Synthesis of monomer 2,7,12-triethynyl-decaethyltruxene (B1)

TBAF in THF (8 mL, 1 mol/L) was added to the mixture of compound **4** (1.8 g, 1.2 mmol) and dichloromethane (10 mL) at 0 ℃, and stirred for 1 h at 0 ℃. The mixture was poured to silica gel and eluted with dichloromethane to afford compound monomer **B1** as a slightly yellow solid (1.51 g, 98%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.31 (d, J=7.8 Hz, 3H), 7.60 (s, 3H), 7.56 (d, J=7.8 Hz, 3H), 3.20 (s, 3H), 2.92—2.86 (m, 6H), 2.10—2.05 (m, 6H), 1.23—1.20 (m, 12H), 1.15—1.11 (m, 12H), 1.09—1.05 (m, 12H), 1.04—0.99 (m, 12H), 0.93—0.89 (m, 18H), 0.86—0.82 (m, 36H), 0.54—0.42 (m, 12H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 153.6, 146.1, 140.7, 137.9, 130.4, 125.9, 124.4, 120.0, 84.4, 55.7, 36.8, 29.7, 29.6, 29.4, 29.3, 23.9, 22.6, 14.1. MALDI-TOF m/z: calcd 1256, found 1255.

General procedure for copper-catalyzed 1,4-regioregular click polymerization

A mixture of monomer **A1**—**A4**, monomer **B1**, THF (5 mL) and H_2O (1 mL) was carefully degassed before fresh aqueous sodium ascorbate (50 μL, 1 mol/L) and fresh aqueous $CuSO_4$ (25 μL, 1 mol/L) were added. The mixture was stirred for hours. The mixture was diluted with methanol, and the precipitate was filtered. The crude polymers were repurified by precipitation from THF into hexane again and dried under vacuum to give polymer.

Synthesis of polymer hb-PTAs1

A1 (36 mg, 12 mmol) and **B** (100 mg, 8 mmol) were used. hb-PTAs1 was obtained as yellow solid (0.11 g, 79%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.45—8.31 (br s, 3H), 8.01—8.00 (br s, 2H), 7.93 (br s, 2H), 7.83 (br s, 2H), 7.58 (br s, 3H), 6.88 (br s, 6H), 4.58 (br s, 3H), 4.03 (br s, 3H), 2.96 (br s, 6H), 2.13 (br s, 9H), 1.64 (br s, 3H), 1.11 (br s, 48H), 0.87 (br s, 54H), 049 (br s, 12H). Anal. calcd for $C_{114}H_{168}N_9O_3$: C 79.95, H 9.89, N 7.36; found C 76.33, H 9.25, N 6.52.

Synthesis of polymer hb-PTAs2

A2 (40 mg, 25 mmol) and **B** (200 mg, 16 mmol) were used. hb-PTAs2 was obtained as yellow solid (0.15 g, 62%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.49 (br s, 3H), 8.19 (br s, 5H), 8.05 (br s, 4H), 7.51 (br s, 3H), 3.05 (br s, 6H), 2.18 (br s, 6H), 1.18 (br s, 48H), 0.89 (br s, 54H), 0.58 (br s, 12H). Anal. calcd for $C_{102}H_{144}N_9$: C 81.87, H 9.70, N 8.42; found C 80.95, H 10.24, N 4.41.

Synthesis of polymer hb-PTAs3

A3 (50 mg, 12 mmol) and **B** (100 mg, 8 mmol) were used. hb-PTAs3 was obtained as yellow solid (0.91 g, 61%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.46 (br s, 6H), 8.14 (br s, 3H), 7.97 (br s, 9H), 7.91 (br s, 2H), 7.50 (br s, 3H), 3.05 (br s, 6H), 2.12 (br s, 12H), 1.96 (br s, 6H), 1.13 (br s, 66H), 0.88 (br s, 63H), 0.59 (br s, 18H). Anal. calcd for $C_{131}H_{186}N_9$: C 83.38, H 9.94, N 6.68; found C 82.41, H 9.87, N 5.23.

Synthesis of polymer hb-PTAs4

A4 (68 mg, 12 mmol) and **B** (100 mg, 8 mmol) were used. hb-PTAs4 was obtained as yellow solid (0.12 g, 71%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.46 (br s, 3H), 8.14 (br s, 3H), 8.00 (br s, 8H), 7.92 (br s, 7H), 7.73 (br s, 9H), 3.02 (br s, 6H), 2.13 (br s, 12H), 1.98 (br s, 6H), 1.11 (br s, 66H), 0.86 (br s, 63H), 0.57 (br s, 18H). Anal. calcd for $C_{149}H_{198}N_9$: C 84.61, H 9.44, N 5.96; found C 82.95, H 9.71, N 3.63.

Results and Discussion

Synthesis of macromonomers and hyperbranched polymers

Monomers diazides A_2 (**A1**—**A4**) and triyne B_3 (structure shown in Scheme 2) containing flexible alkyl chains were designed to realize the planned A_2+B_3 approach to hb-PTAs. All the monomers can be facilely taken into consideration by click polymerizations with Cu(I)-catalyst, and the hyperbranched polymers from the designed monomers were easily soluble in common solution such as dichloromethane, toluene and THF *etc*. The synthetic routes to monomers are outlined in Scheme 3. the monomers (**A1**—**A4**) were synthesized by substitution reaction with sodium azide from the amine precursors, 2,7-diamine-9,9-dihexylfluorene was obtained by two step reaction of nitration and reduction from the 9,9-dihexylfluorene in good yields of 82% and 94%; the compound **3** was synthesized by Suzuki cou-

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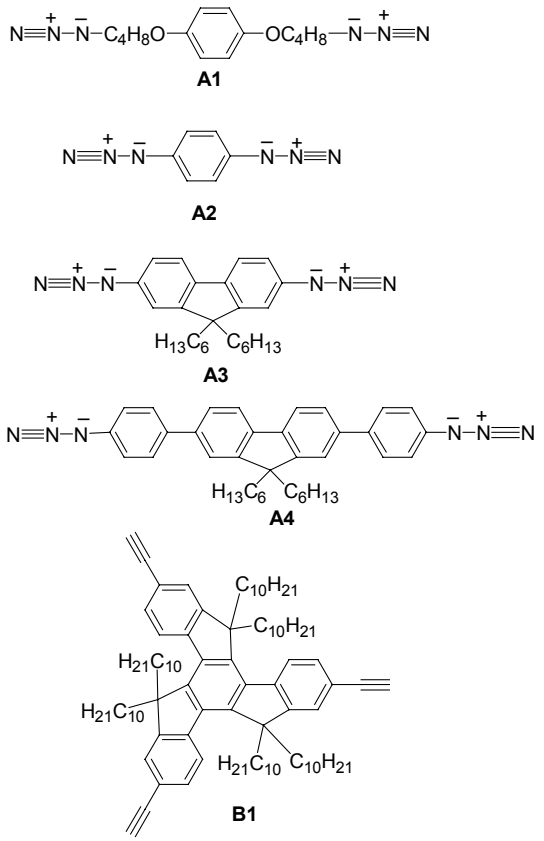
pling reaction with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene and *N*-(*t*-butoxycarbonyl)-1-amino-4-bromobenzene in yield of 81%, and after removing the Boc-group, the intermediate was directly used in the next diazotization reaction, finally substituted by sodium azide to afford monomer **A4** in total yield of 80%. The monomer **B1** was prepared by coupling with (trimethylsilyl)acetylene and base-catalyzed disilylation and unprotecting trimethylsilyl group in high yields of 90% and 98%.

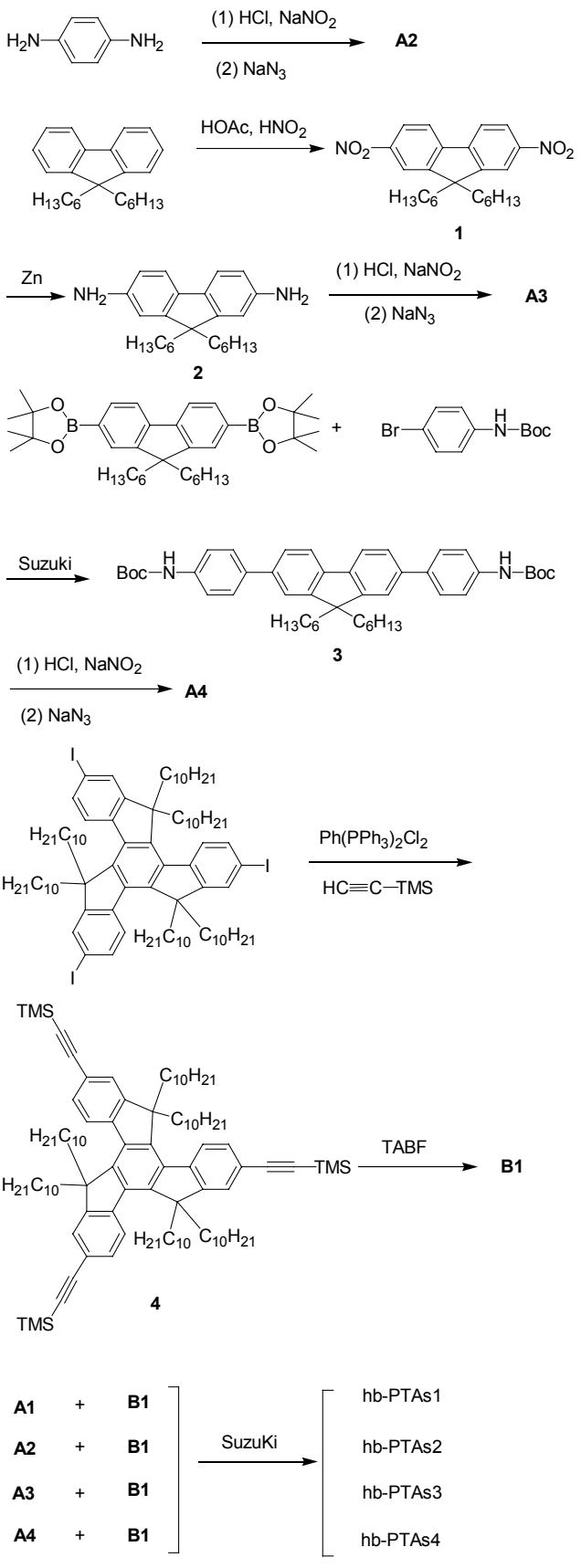
Scheme 2 Structures of monomers **A1**—**A4**, and **B1**



1,3-Dipolar polycycloadditions of diazides and triyne

The click polycycloadditions can be brought out by using thermal polymerizations and the Cu(I), Ru(II) catalyzed polymerizations, to prepare regioregular polymers at a fast rate. We paid attention to the metal catalysts used in the azide-alkyne click reactions. In our work the $CuSO_4$/sodium ascorbate catalyst in a THF/water mixture was used to prepared the hyperbranched polymers. The incompatibility between the growing hb-PTA species and the aqueous medium may have induced the polymers to aggregate and hence precipitate. In fact all the polymers were precipitated from the THF/water mixture, otherwise the polymers hb-PTAs1 and hb-PTAs2 can be mostly soluble in common solution, the polymers hb-PTAs3 and hb-PTAs4 are all soluble in common solution, and the molecule weights were high. The click polycycloadditions were brought out under the standard click reaction

Scheme 3 Synthesis of monomers and hypbranched polymers hb-PTAs **(1—4)**



conditions, the molar ratio of the A_2 and B_3 was 3∶2. Its M_n, M_w and PDI values were estimated by GPC calibrated by linear polystyrene standards. The yields of polymers hb-PTAs (**1**—**4**) were 58%, 76%, 63% and 75%, respectively. The molecular structure of the polymers was verified by ^{1}H NMR spectroscopy, MALDI-TOF and elemental analysis.

The IR spectra of hb-PTAs (**1**—**4**) polymers are shown in Figure 1; those of monomers **A3** and **B1** are given in the figure for comparison. Monomer **B1** absorbs at 3299 and 2104 cm^{-1} due to its ≡C—H and C≡C stretching vibrations, respectively. Monomer **A3** exhibits a strong absorption band at 2094 cm^{-1} associated with the stretching of its azido group. All these absorption bands become weaker in intensity in the spectrum of hb-PTAs1, and become nearly invisible in the spectra of higher molecular weight polymers hb-PTAs2, hb-PTAs3 and hb-PTAs4. This suggests that most of the ethynyl and azido groups of the monomers have been transformed to the triazole rings of the polymer by the polymerization reaction.

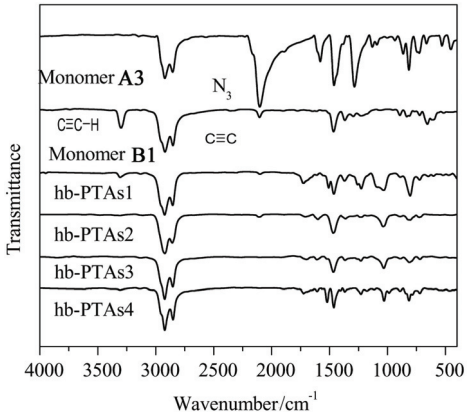


Figure 1 IR spectra of hypbranched polymers hb-PTAs (**1**—**4**).

The molecule test and thermal properties

The molecular weights of polymers hb-PTAs (**1**—**4**) were determined by gel permeation chromatography (GPC) with THF as the eluent, calibrated against polystyrene standards. As shown in Table 1 and Figure 2, the GPC analysis indicated that the number-average molecular weight (M_n) and polydispersity index of the polymers are in the ranges (1.2—3.3)×10^4 and 1.7—3.0, respectively. The elution curve of polystyrene standards (M_n=30300) was given in the Figure 2 as an example.

The thermal properties of the hyperbranchced ladder type polymers hb-PTAs (**1**—**4**) were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere. All polymers exhibited good thermal stability with onset degradation temperatures (T_d) above 330 ℃ (Figure 3). Neither a glass transition process (T_g) nor other thermal processes (such as liquid crystal phase) were observed from 25 to 300 ℃ in the DSC trace of second heating (10 ℃/min).

Table 1 Physical properties of hypbranched ladder type polymers hb-PTAs (**1**—**4**)

Polymer	M_n	M_w	PDI	T_d/℃
hb-PTAs1	12300	24800	2.16	373
hb-PTAs2	22300	67300	3.00	351
hb-PTAs3	27300	47600	1.74	360
hb-PTAs4	33400	87200	2.61	342

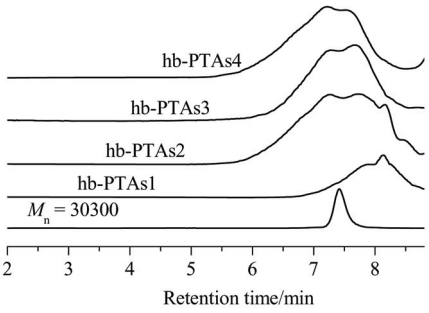


Figure 2 GPC elution traces of hypbranched polymers hb-PTAs (**1**—**4**) and standard (M_n=30300).

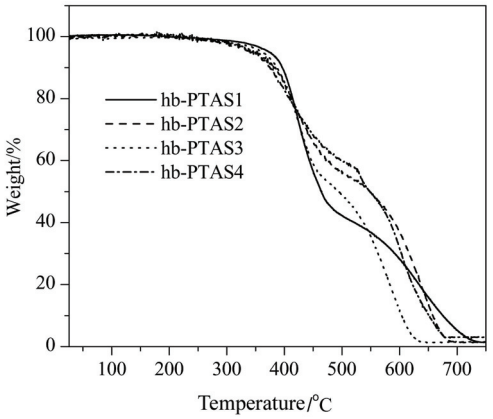


Figure 3 TGA traces of hypbranched polymers hb-PTAs (**1**—**4**).

Optical properties

Figure 4 shows the absorption and PL spectra of the hyperbranched polymers in dilute solution of chloroform. The polymer hb-PTAs1 exhibited an absorption and emission band with the maximum at about 326 and 381 nm, the polymers hb-PTAs (**2**—**4**) exhibited similar absorption that were broad and peaked at around 335, 337 and 340 nm, respectively, the absorption maxima slightly red-shifted with the increasing linear length. The polymer hb-PTAs2 exhibited an emission band in the blue region with the peak at 382 nm with a shoulder at 483 nm, the polymer hb-PTAs3 shows broad blue emission with two peaks at 382 and 403 nm, the polymer hb-PTAs4 exhibited the blue emission band with two peaks at 382 and 402 nm with a shoulder at 462 nm. All the emission peaks of the polymers in solution show no obvious change.

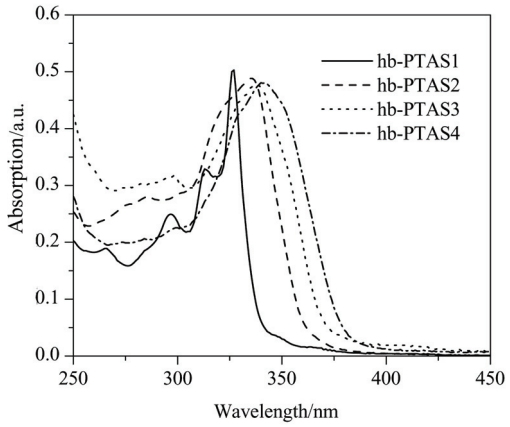


Figure 4 UV-Vis absorption and PL spectra of hypbranched polymers hb-PTAs (**1**—**4**) in chloroform.

Solid films of polymers hb-PTAs (**1**—**4**) on quartz plates used for UV-Vis and fluorescence were prepared by spin-coating from a 10 mg/mL THF solution at 1500 r/min. The UV-Vis and photoluminescence spectra of hb-PTAs (**1**—**4**) are shown in Figure 5. In contrast to their solution spectra, the absorption bands of hb-PTAs (**1**—**4**) in thin film were slightly broader and red-shifted about 4 nm, and significant differences were observed between the film and solution photoluminescence spectra of the polymers hb-PTAs (**1**—**4**), which can be attributed to the change in the conformation. In the reported literature all the polymers were nearly nonfluorescent in the solid state, although their dilute solutions emitted UV light, suggesting that the polymer luminescence was quenched by aggregate formation. The hyperbranched polymer hb-PTAs (**1**—**4**) exhibited an emission band in the blue region with the peak at about 360 nm, but an evident low energy band at 470 nm is stronger than in solution. The results showed that the hyperbranched structure can minimize this tendency for aggregation, but there still exist aggregations in the film.

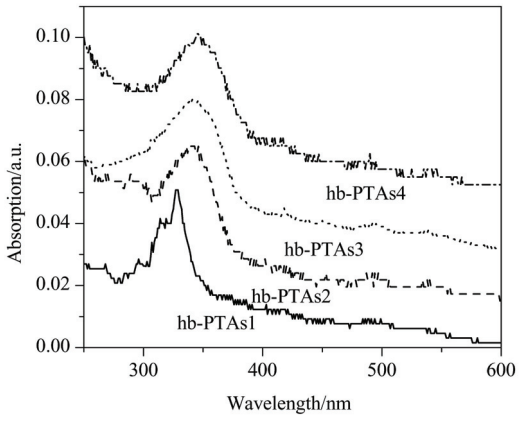


Figure 5 UV-Vis absorption and PL spectra of hypbranched polymers hb-PTAs **(1—4)** in film.

Conclusions

We have successfully prepared a series of hyperbranched polymers (hb-PTAs1, hb-PTAs, hb-PTAs, and hb-PTAs) via the Cu(I)-catalyzed click reaction by an "A_2+B_3" approach. These hyperbranched polymers are soluble in common organic solvents, and their number-average molecular weight (M_n) values were (1.2—3.3)$\times 10^4$ g/mol with polydispersity indexes (PDI) being in the range of 1.7—3.0. All the polymers exhibited good thermal stability with onset degradation temperatures (T_d) above 330 ℃ (Figure 3). Neither a glass transition process (T_g) nor other thermal processes (such as liquid crystal phase) were observed from 25 to 300 ℃ in the DSC trace. All the polymers give strong blue emission in solutions, and evident aggregations were observed in film states.

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