Hyperbranched Polytriazoles: Click Polymerization, Regioisomeric Structure, Light Emission, and Fluorescent Patterning

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Experimental Section

General Information. THF (Labscan), toluene (BDH) and dioxane (Aldrich) were distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Other commercially available reagents and solvents were all purchased from Aldrich and used as received without further purification.

All spectral data were measured at room temperature unless otherwise specified. ^{1}H and ^{13}C NMR spectra were taken on a Bruker ARX 300 spectrometer using chloroform-*d* or DMSO-d_6 as solvent and tetramethylsilane (TMS; $\delta = 0$) as internal reference. IR spectra were recorded on a Perkin-Elmer 16 PC spectrometer. UV-vis absorption spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Emission spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Fluorescence quantum yield (Φ_F) in dichloromethane (DCM) was estimated using 9,10-diphenylanthracene in cyclohexane ($\Phi_F = 90\%$) as standard. Thermal stability was evaluated on a Perkin-Elmer thermogravimetric analyzer TGA 7 under nitrogen at a heating rate of 20 ^{o}C/min. Thermal transitions were measured by differential scanning calorimetry (DSC) using a DSC Q1000 instrument at a heating rate of 10 °C/min under nitrogen.

Relative weight- ($M_{w,r}$) and number-average ($M_{n,r}$) molecular weights and polydispersity indices (PDI) of the *hb*-PTA polymers were estimated by a Waters 510 gel permeation chromatography (GPC) system equipped with refractive index (RI) and UV detectors. THF was used as eluent at a flow rate of 1.0 mL/min. A set of linear polystyrene standards was used for the molecular weight calibration. Absolute molecular weights of the *hb*-PTAs were measured by laser light scattering (LLS) technique.[1] Dynamic and static LLS data were taken on Brookhaven Instruments BI-200SM Goniometer with a BI-TurboCorr Digital Correlator. Vertically polarized light was supplied by a solid-state laser source (CNI Changchun GXL-III, 532 nm, 100 mW). The sample cell was placed in a thermostatic bath at 25 °C with a temperature accuracy of ±0.01 °C. To measure specific refractive index increment (d*n*/d*C*) value, the polymer solutions in THF (for *hb*-*r*-P**1**) or DMF (for *hb*-1,5-P**1**) with different concentrations were filtered through Millipore 0.22 μm PTFE filters into dust-free vials, and static LLS measurements were performed in the angular range of 20–120°. In the dynamic LLS measurements, autocorrelation function was collected at 30, 60 and 90° in the homodyne mode using Brookhaven Instrument software of 9KLDSW. Time correlation functions were analyzed with a Laplace inversion program CONTIN.

Syntheses of Monomers. Tris(4-ethynylphenyl)amine **3** was prepared using published procedures[2] and purified by a silica gel column using a mixture of hexane/chloroform (2:1 by volume) as eluent (R_f = 0.66). IR (KBr), ν (cm^{-1}): 3287, 2104, 1598, 1497, 1318, 833. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.39 (d, 6H), 7.02 (d, 6H), 3.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 147.1, 133.5, 124.0, 117.0, 83.5, 77.1. HRMS (MALDI–TOF) *m*/*z* Calcd: 317.1204. Found: 317.1198 (M^+).

Diazides **2** and monoazides **8** were prepared according to the synthetic routes shown in Schemes 2 and 3, respectively. Typical experimental procedures for the synthesis of diazide **2b**, namely 1,4-bis(6-azidohexyloxy)benzene, are given below as an example.

Into a 250 mL round-bottom flask was added 1,6-dibromohexane (16.8 g, 66 mmol) and K_2CO_3 (20.7 g, 150 mmol) in 100 mL of acetone. Hydroquinone **4** (3.3 g, 30 mmol) in 25 mL of acetone was added into the flask dropwise within 4 h under reflux. The mixture was further refluxed for 12 h and then cooled to room temperature. The inorganic salt was filtered and washed with acetone several times. The filtrate was concentrated by a rotary evaporator and the residue was extracted with 200 mL of chloroform. The organic phase was washed with 50 mL of water three times and 100 mL of brine once and then dried over $MgSO_4$ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using a chloroform/hexane mixture (1:1 by volume) as eluent (R_f = 0.73). A white solid of 1,4-bis(6-bromohexyloxy)benzene **5b** was obtained in 70.5% yield (9.16 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.81 (s, 4H), 3.91 (t, 4H), 3.42 (t, 4H), 1.89 (m, 4H), 1.77 (m, 4H), 1.50 (m, 8H).

Into another 250 mL round-bottom flask were added **5b** (3.05 g, 7 mmol) and sodium azide (1.14 g, 17.5 mmol) in 100 mL of DMSO. After stirring at room temperature for 24 h, a small amount of water was added to quench the reaction (temperature of the solution being raised slightly). After cooled to room temperature, the solution was extracted with 30 mL of diethyl ether five times. The organic layers were combined, washed with water and brine, and dried over $MgSO_4$ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using a chloroform/hexane mixture (1:1 by volume) as eluent (R_f = 0.61). Monomer **2b** was obtained in 89.3% yield (2.25 g) as a white solid. IR (KBr), ν (cm^{-1}): 2097, 1509, 1469, 1231, 827. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.82 (s, 4H), 3.91 (t, 4H), 3.28 (t, 4H), 1.77 (m, 4H), 1.63 (m, 4H), 1.47 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 153.8, 116.0, 69.0, 52.0, 29.9, 29.4, 27.1, 26.3. HRMS (MALDI–TOF): m/z Calcd: 360.2274. Found: 360.2270 (M^+).

Monomer **2a** and compounds **8a** and **8b** were prepared by the experimental procedures similar to those described above. Their characterization data were given below.

*1,4-Bis(4-azidobutoxy)benzene (**2a**):* Purified by a silica gel column using a chloroform/hexane mixture (1:1 by volume) as eluent (R_f = 0.56). White solid; yield 32.0% (based on the amount of hydroquinone **4** used). IR (KBr), ν (cm^{-1}): 2097, 1508, 1472, 1229, 827. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.82 (s, 4H), 3.94 (t, 4H), 3.36 (t, 4H), 1.82 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 153.7, 68.4, 51.8, 27.2, 26.4. HRMS (MALDI–TOF) m/z Calcd: 304.1648. Found: 304.1650 (M^+).

*1-(4-Azidobutoxy)benzene (**8a**):* Purified by a silica gel column using a hexane/chloroform mixture (3:1 by volume) as eluent (R_f = 0.65). Colorless oil; yield 61.7% (based on the amount of phenol **6** used). IR (KBr), ν (cm^{-1}): 2096, 1600, 1497, 1472, 1244, 754, 691. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.28 (m, 2H), 6.94 (m, 3H), 3.98 (t, 2H), 3.36 (t, 2H), 1.83 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.5, 130.2, 121.4, 115.1, 67.7, 51.9, 27.2, 26.5.

*1-(6-Azidohexyloxy)benzene (**8b**):* Purified by a silica gel column using a hexane/chloroform mixture (3:1 by volume) as eluent (R_f = 0.65). White solid; yield 67.6% (based on the amount of phenol **6** used). IR (KBr), ν (cm^{-1}): 2094, 1600, 1497, 1470, 1244, 753, 691. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.26 (m, 2H), 6.90 (m, 3H), 3.93 (t, 2H), 3.24 (t, 2H), 1.77 (m, 2H), 1.63 (m, 2H), 1.44 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.7, 130.1, 121.2, 115.1, 68.2, 52.0, 29.8, 29.5, 27.2, 26.4.

Preparations of Model Compounds. Regioregular 1,4- (**9**) and 1,5-disubstituted (**10**) 1,2,3-triazole compounds were prepared by the model reactions shown in Scheme 4.

Model compounds **9** were synthesized by the copper-catalyzed click reactions of **3** and **8**. Into a 30 mL Schlenk tube were added tris(4-ethynylphenyl)amine **3** (0.2 g, 0.63 mmol) and 1-(4-azidobutoxy)-benzene **8a** (0.47 g, 2.46 mmol) in 5 mL of THF. After the monomers were completely dissolved, 1 mL of water and freshly prepared aqueous solutions of sodium ascorbate (1 M, 190 µL, 10 mol %) and $CuSO_4$ (1 M, 95 µL, 5 mol %) were added subsequently under vigorous stirring. The color of the solution turned to brown, orange and then yellow. The reaction mixture was stirred at room temperature overnight. THF was evaporated and the residue was extracted with 20 mL of chloroform. The organic layer was washed sequentially with 5 mL of saturated ammonium chloride aqueous solution, 20 mL of water and 20 mL of brine, and then dried over anhydrous sodium sulfate overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using an ethyl acetate/hexane mixture (2:1 by volume) as eluent (R_f = 0.41). A white solid of **9a** was obtained in 54.0% yield (0.3 g). IR (KBr), v (cm^{-1}): 1600, 1586, 1557, 1495, 1245, 830, 755, 692. ^1H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 8.65 (s, 3H), 7.91 (d, 6H), 7.37 (t, 6H), 7.25 (d, 6H), 7.03 (m, 9H), 4.57 (t, 6H), 4.09 (t, 6H), 2.13 (m, 6H), 1.81 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.3, 148.2, 147.8, 130.2, 127.4, 126.0, 125.1, 121.5, 119.7, 115.1, 67.4, 50.7, 28.0, 26.9. MS (MALDI-TOF): m/z Calcd: 890.40. Found: 891.41 $(M + H)^+$. Anal. Calcd for $C_{54}H_{54}N_{10}O_3$: C, 72.79; H, 6.11; N, 15.72. Found: C, 72.18; H, 6.10; N, 15.10.

Compound **9b** was prepared by similar procedures and purified by a silica gel column (R_f = 0.54). White solid; yield 37.9%. IR (KBr), v (cm^{-1}): 1600, 1585, 1557, 1496, 1244, 838, 755, 692. ^1H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 8.64 (s, 3H), 7.90 (d, 6H), 7.35 (t, 6H), 7.25 (d, 6H), 7.00 (m, 9H), 4.50 (t, 6H), 4.03 (t, 6H), 1.99 (m, 6H), 1.80 (m, 6H), 1.55 (m, 6H), 1.44 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.6, 148.1, 147.8, 130.1, 127.4, 126.1, 125.1, 121.3, 119.6, 115.1, 68.1, 51.0, 31.0, 29.7, 26.9, 26.3. MS (MALDI-TOF): m/z Calcd: 974.53. Found: 975.49 $(M + H)^+$. Anal. Calcd for $C_{60}H_{66}N_{10}O_3$: C, 73.89; H, 6.82; N, 14.36. Found: C, 73.28; H, 6.76; N, 14.41.

Model compounds **10** were prepared using Cp*Ru$(PPh_3)_2$Cl as catalyst. Tris(4-ethynylphenyl)amine **3** (0.063 g, 0.2 mmol), 1-(4-azidobutoxy)benzene **8a** (0.15 g, 0.8 mmol), and Cp*Ru$(PPh_3)_2$Cl (9.7 mg, 2 mol %) were added into a 20 mL Schlenk tube. The tube was evacuated and refilled with nitrogen three times. THF (1.5 mL) was injected into the tube to dissolve the reactants. The mixture was stirred at 60 ^{o}C for 2 h. After cooled to room temperature, the solvent was evaporated and the crude product was purified by a silica gel column using ethyl acetate as eluent (R_f = 0.69). A light yellow solid of **10a** was obtained in 84.3% yield (0.15 g). IR (KBr), ν (cm^{-1}): 1601, 1586, 1557, 1490, 1244, 830, 755, 692. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 7.98 (s, 3H), 7.61 (d, 6H), 7.33 (t, 6H), 7.25 (d, 6H), 6.95 (m, 9H), 4.59 (t, 6H), 4.00 (t, 6H), 2.03 (m, 6H), 1.78 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.3, 148.3, 137.8, 133.7, 130.6, 130.2, 125.3, 122.9, 121.5, 115.0, 67.4, 48.7, 27.6, 26.9. MS (MALDI-TOF): *m*/*z* Calcd: 890.40. Found: 891.42 (M + H)$^+$. Anal. Calcd for $C_{54}H_{54}N_{10}O_3$: C, 72.79; H, 6.11; N, 15.72. Found: C, 72.71; H, 6.19; N, 15.23.

Compound **10b** was prepared by similar procedures and purified by a silica gel column using an ethyl acetate/hexane mixture (2:1 by volume) as eluent (R_f = 0.75). Light yellow viscous oil; yield 79.3%. IR (KBr), ν (cm^{-1}): 1601, 1586, 1557, 1490, 1244, 830, 755, 692. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 7.95 (s, 3H), 7.62 (d, 6H), 7.33 (m, 12H), 6.96 (m, 9H), 4.50 (t, 6H), 3.97 (t, 6H), 1.85 (m, 6H), 1.71 (m, 6H), 1.43 (m, 6H), 1.34 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.6, 148.3, 137.7, 133.7, 130.6, 130.1, 125.3, 123.0, 121.3, 115.1, 68.1, 48.9, 30.7, 29.7, 26.9, 26.2. MS (MALDI-TOF): *m*/*z* Calcd: 974.53. Found: 975.46 (M + H)$^+$.

Model compounds of 1,4-regioregular 1,2,3-triazoles **11** and **12** were prepared by the reactions shown in Scheme 5.

Compound **11** was prepared by Cu(I)-catalyzed click reaction of 4-ethynyl-*N,N*-diphenylbenzenamine (**13**) and 1,4-bis(6-azidohexyloxy)benzene (**2b**). Into a 30 mL Schlenk tube were added **13** (81 mg, 0.3 mmol) and **2b** (110 mg, 0.3 mmol) in 5 mL of THF. After the reactants were completely dissolved, 1 mL of water and freshly prepared aqueous solutions of sodium ascorbate (1 M, 100 µL, 10 mol %) and $CuSO_4$ (1 M, 50 µL, 5 mol %) were added subsequently under vigorous stirring. The color of the solution turned to brown, orange and then yellow. The reaction mixture was stirred at room temperature overnight. THF was evaporated and the residue was extracted with 30 mL of chloroform. The organic layer was washed sequentially with 10 mL of saturated ammonium chloride aqueous solution, 30 mL of water and 30 mL of brine, and then dried over sodium sulfate overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using an ethyl acetate/hexane mixture (2:1 by volume) as eluent. A yellow solid of compound **11** was obtained in 28.0% yield (53 mg). IR (KBr), ν (cm^{-1}): 2094, 1591, 1504, 1278, 1228, 825, 755, 697. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.70 (s, 1H), 7.65 (d, 2H), 7.25 (t, 4H), 7.12 (m, 6H), 7.03 (m, 2H), 6.81 (s, 4H), 4.39 (t, 2H), 3.89 (m, 4H), 3.27 (t, 2H), 1.97 (m, 2H), 1.75 (m, 6H), 1.63 (m, 2H), 1.46 (m, 8H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 153.7, 153.6, 148.2, 148.0, 129.8, 127.1, 125.2, 124.9, 124.2, 123.5, 119.3, 115.9, 68.8, 68.7, 51.9, 50.7, 30.7, 29.7, 29.6, 29.3, 27.0, 26.7, 26.1, 26.0. MS (ESI): *m*/*z* Calcd: 629.3. Found: 630.3 (M + H)$^+$. Anal. Calcd for $C_{38}H_{43}N_7O_2$: C, 72.47; H, 6.88. Found: C, 72.67; H, 7.16.

Compound **12** was synthesized by the click reaction of phenylacetylene **14** (102 mg, 1.0 mmol) and 1-(6-azidohexyloxy)benzene **8b** (220 mg, 1.0 mmol) by the similar experimental procedures. A white solid of compound **12** was obtained in 87.5% yield (281.4 mg). IR (KBr), ν (cm^{-1}): 1600, 1586, 1463, 1247, 1215, 1078, 750, 694. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.81(d, 2H), 7.73 (s, 1H), 7.42 (m, 2H), 7.32 (m, 1H), 7.25 (m, 2H), 6.93 (d, 1H), 6.89 (m, 2H), 4.41 (t, 2H), 3.96 (t, 2H), 1.99 (m, 2H), 1.76 (m, 2H), 1.55 (m, 2H), 1.48 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 159.4, 148.2, 130.8, 129.9, 129.3, 128.6, 126.2, 121.1, 119.8, 114.9, 67.9, 50.8, 30.8, 29.5, 26.7, 26.1. MS (CI): *m*/*z* Calcd: 321.2. Found: 322.2 (M + H)$^+$. Anal. Calcd for $C_{20}H_{23}N_3O$: C, 74.74; H, 7.21. Found: C, 74.57; H, 7.32.

Characterization Data for the Polymers. *Regiorandom Polymer hb-r-P**1a***: Yellow powder; yield 64.0%. $M_{w,r}$ 5500, M_w/M_n 2.0 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3283, 2097, 1606, 1557, 1506, 1227, 825. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 8.63, 8.00, 7.48, 7.21, 7.09, 6.93, 6.87, 4.54, 4.21, 4.00, 3.92, 2.08, 2.01, 1.74. ^{13}C NMR (75 MHz, DMSO-d_6), δ (TMS, ppm):

152.5, 145.9, 136.9, 133.1, 132.5, 129.7, 127.0, 126.5, 125.5, 124.8, 123.8, 123.4, 122.6, 121.0, 115.2, 83.4, 80.1, 67.1, 50.4, 49.3, 47.5, 26.5, 26.2, 26.0, 25.8, 25.6, 25.1, 24.7.

*Regiorandom Polymer hb-r-P**1b***: Yellow powder; yield 75.7%. $M_{\mathrm{w,r}}$ 11400, $M_{\mathrm{w}}/M_{\mathrm{n}}$ 2.7 (GPC, polystyrene calibration); $M_{\mathrm{w,a}}$ 177500 (LLS). IR (KBr), ν (cm^{-1}): 3286, 2095, 1601, 1556, 1506, 1491, 1228, 824. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 8.60, 7.89, 7.51, 7.23, 7.09, 6.86, 4.47, 4.21, 3.88, 1.95, 1.83, 1.72, 1.63, 1.45, 1.39, 1.32. ^{13}C NMR (75 MHz, DMSO-d_6), δ (TNS, ppm): 152.5, 147.4, 146.7, 146.0, 136.7, 132.7, 132.3, 129.2, 126.5, 126.4, 125.0, 124.5, 124.3, 123.8, 123.2, 123.0, 122.8, 118.6, 115.0, 82.9, 67.8, 56.3, 50.8, 49.7, 47.6, 29.7, 29.4, 28.6, 28.5, 28.2, 25.9, 25.7, 25.1, 24.9.

*1,4-Regioregular Polymer hb-1,4-P**1a***: Yellowish-white solid; yield 46.3%. $M_{\mathrm{w,r}}$ 5600, $M_{\mathrm{w}}/M_{\mathrm{n}}$ 1.5 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3283, 2098, 1599, 1558, 1507, 1320, 1286, 1228, 834. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 8.64, 7.89, 7.49, 7.22, 7.08, 6.93, 4.56, 4.20, 4.00, 3.48, 2.11, 1.78. ^{13}C NMR (75 MHz, DMSO-d_6), δ (TMS, ppm): 152.5, 147.3, 146.8, 146.0, 145.9, 145.8, 145.4, 135.0, 133.1, 132.0, 131.4, 129.9, 128.8, 127.0, 126.4, 125.5, 124.8, 124.0, 123.1, 122.2, 121.0, 115.8, 115.3, 83.4, 80.2, 67.1, 50.4, 49.2, 26.5, 26.0, 25.7, 25.1.

*1,4-Regioregular Polymer hb-1,4-P**1b***: Yellow powder; yield 51.6%. $M_{\mathrm{w,r}}$ 5000, $M_{\mathrm{w}}/M_{\mathrm{n}}$ 2.0 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3288, 2097, 1599, 1557, 1506, 1320, 1285, 1228, 835. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 8.63, 7.88, 7.49, 7.21, 7.08, 6.89, 4.49, 4.20, 3.95, 3.40, 1.97, 1.75, 1.62, 1.42. ^{13}C NMR (75 MHz, DMSO-d_6), δ (TMS, ppm): 152.5, 147.3, 146.8, 146.3, 145.9, 145.7, 145.3, 135.0, 133.4, 133.1, 131.4, 130.1, 129.9, 128.7, 127.0, 126.4, 125.5, 124.8, 124.0, 123.1, 122.1, 120.9, 115.8, 115.2, 83.4, 80.2, 67.7, 65.3, 50.5, 49.4, 29.5, 28.5, 28.2, 25.9, 25.5, 24.9, 19.9.

*1,5-Regioregular Polymer hb-1,5-P**1a***: Greenish-yellow powder; yield 84.5%. $M_{\mathrm{w,r}}$ 5400, $M_{\mathrm{w}}/M_{\mathrm{n}}$ 2.4 (GPC, polystyrene calibration); $M_{\mathrm{w,a}}$ 72800 (LLS). IR (KBr), ν (cm^{-1}): 3287, 2947, 2871, 2097, 1606, 1507, 1490, 1228, 825. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 7.92, 7.49, 7.20, 6.80, 4.54, 4.21, 3.88, 1.98, 1.70. ^{13}C NMR (75 MHz, DMSO-d_6), δ (TMS, ppm): 152.5, 146.8, 136.8, 133.2, 132.5, 124.1, 123.7, 123.4, 121.7, 116.3, 115.2, 83.3, 80.4, 67.2, 67.0, 66.8, 50.5, 47.5, 47.2, 26.1, 26.0, 25.6, 25.1, 24.6.

*1,5-Regioregular Polymer hb-1,5-P**1b***: Light yellow powder; yield 74.9%. $M_{\mathrm{w,r}}$ 9400, $M_{\mathrm{w}}/M_{\mathrm{n}}$ 2.7 (GPC, polystyrene calibration); $M_{\mathrm{w,a}}$ 32200 (LLS). IR (KBr), ν (cm^{-1}): 3286, 2939, 2862, 2095, 1606, 1507, 1490, 1229, 825. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 7.92, 7.65, 7.19, 6.80, 4.46, 4.21, 3.84, 3.38, 1.80, 1.61, 1.33. ^{13}C NMR (75 MHz, DMSO-d_6), δ (TMS, ppm):152.4, 146.8, 136.7, 133.2, 132.4, 129.8, 124.2, 123.7, 121.8, 115.4, 115.0, 83.2, 80.3, 67.6, 50.6, 47.6, 29.1, 28.6, 28.4, 28.2, 27.5, 25.9, 25.4, 25.0, 24.7.

Degree of Branching (DB) for *hb*-*r*-P1a. Following the discussion for the DB calculation for *hb*-*r*-P**1b**, we can derive the following equation for its counterpart with a shorter alkyl chain length, *hb*-*r*-P**1a**:

$$f_{\mathrm{La}} + 2f_{\mathrm{Taa}} = 0.34 \qquad \text{(S1)}$$

In the 1,3-dipolar polycycloaddition, it is reasonable to assume $f_{\mathrm{Taa}} \geq 0$, from which we get $f_{\mathrm{La}} \leq 0.34$.

According to definition, DB of *hb*-*r*-P**1a** can be expressed as:

$$\mathrm{DB} = \frac{f_{\mathrm{D}} + f_{\mathrm{Te}} + f_{\mathrm{Taa}} + f_{\mathrm{Tea}}}{f_{\mathrm{D}} + f_{\mathrm{Le}} + f_{\mathrm{La}} + f_{\mathrm{Tee}} + f_{\mathrm{Taa}} + f_{\mathrm{Tea}}} \qquad \text{(S2)}$$

Incorporating eq 5 and $f_{\mathrm{La}} \leq 0.34$ into eq 2 gives the following DB value for *hb*-*r*-P**1a**:

$$DB = 1 - f_{\mathrm{Le}} - f_{\mathrm{La}} \geq 1 - 0.03 - 0.34 \ (\mathrm{DB} \geq 0.63) \qquad \text{(S3)}$$

According to Chart 2, the following relationship holds:

$$\frac{f_{\mathrm{Taa}}}{f_{\mathrm{La}}} = 2 \qquad \text{(S4)}$$

Combining eqs S1 and S4, we can obtain:

$$f_{\mathrm{La}} = 0.07 \qquad \text{(S5)}$$

Eventually, under the proposed assumptions and within experimental errors, the DB value of *hb*-*r*-P**1a** is deduced to be:

$$\mathrm{DB} = 1 - f_{\mathrm{Le}} - f_{\mathrm{La}} = 1 - 0.03 - 0.07 = 0.90 \qquad \text{(S6)}$$

Model Photolysis Reactions. The photolysis experiments were performed by irradiating the solutions of the model compounds in acetonitrile with a 200-W Hg lamp (Oriel) at a distance of ~5 cm from the sample solutions under stirring.

Photolysis of Model Compound ***8b***. The azide compound (40 mg) was dissolved in acetonitrile (40 mL) and the resultant solution was irradiated by the UV lamp for 10 h. The compound was photolyzed and oxidized, as revealed by the disappearance of the resonance peaks of the protons of the methylene unit adjacent to the azido group and by the appearance of the resonance signal of an aldehyde proton in the NMR spectrum of the reaction product (cf., Figure 9).

Photolysis of Model Compound ***11***. The solution of azidotriazole compound (60 mg) in acetonitrile (60 mL) was irradiated by the UV lamp. After 12 h irradiation, the color of the solution changed from light yellow to reddish yellow. The photolysis products precipitated out from the solution, which were insoluble in common organic solvents such as DCM, THF, DMF and DMSO.

Attempted Photolysis of Model Compound ***12***. The solution of the triazole compound (60 mg) in acetonitrile (60 mL) was irradiated by the UV lamp. No change in the structure of **11** was detected by TLC and NMR analyses after 12 h irradiation, indicating that photolysis reaction had not occurred or that the triazole ring is photochemically stable.

References and Notes

(1) (a) Chu, B. *Laser Light Scattering*; Academic Press: New York, 1991. (b) Yu, Z.-Q.; Liu, J.-H.; Yan, J.-J.; Liu, X.-B.; Liang, D.-H.; Lam, J. W. Y.; Dong, Y.-P.; Li, Z.-C.; Chen, E.-Q.; Tang, B. Z. *Macromolecules* **2007**, *40*, 8342. (c) Xu, K.; Peng, H.; Sun, Q.; Dong, Y.; Salhi, F.; Luo, J.; Chen, J.; Huang, Y.; Zhang, D.; Xu, Z.; Tang, B. Z. *Macromolecules* **2002**, *35*, 5821.

(2) (a) Zheng, R.; Häußler, M.; Dong, H.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **2006**, *39*, 7973. (b) Häußler, M.; Zheng, R.; Lam, J. W. Y.; Tong, H.; Dong, H.; Tang, B. Z. *J. Phys. Chem. B* **2004**, *108*, 10645.

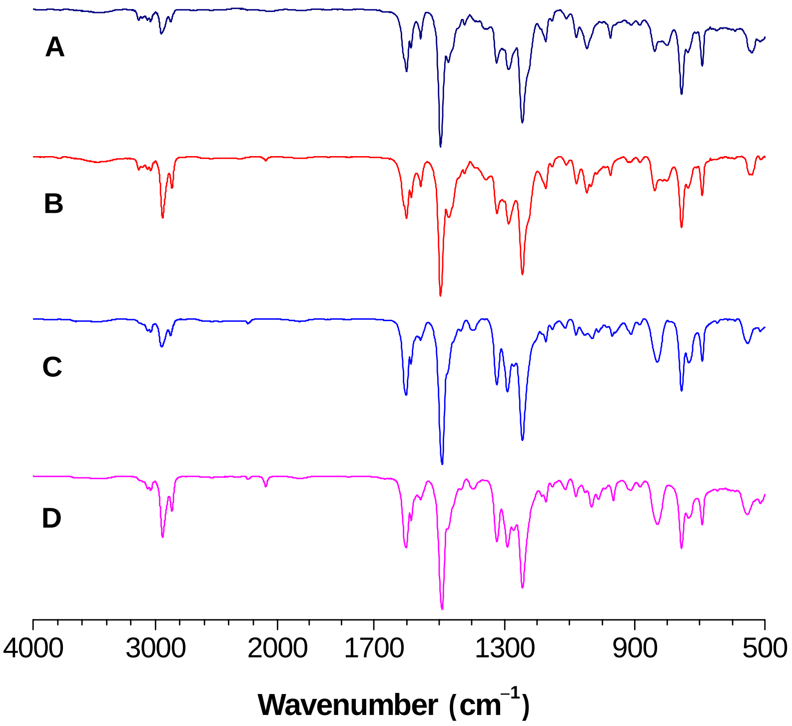


Figure S1. IR spectra of model compounds (A) **9a**, (B) **9b**, (C) **10a** and (D) **10b**.

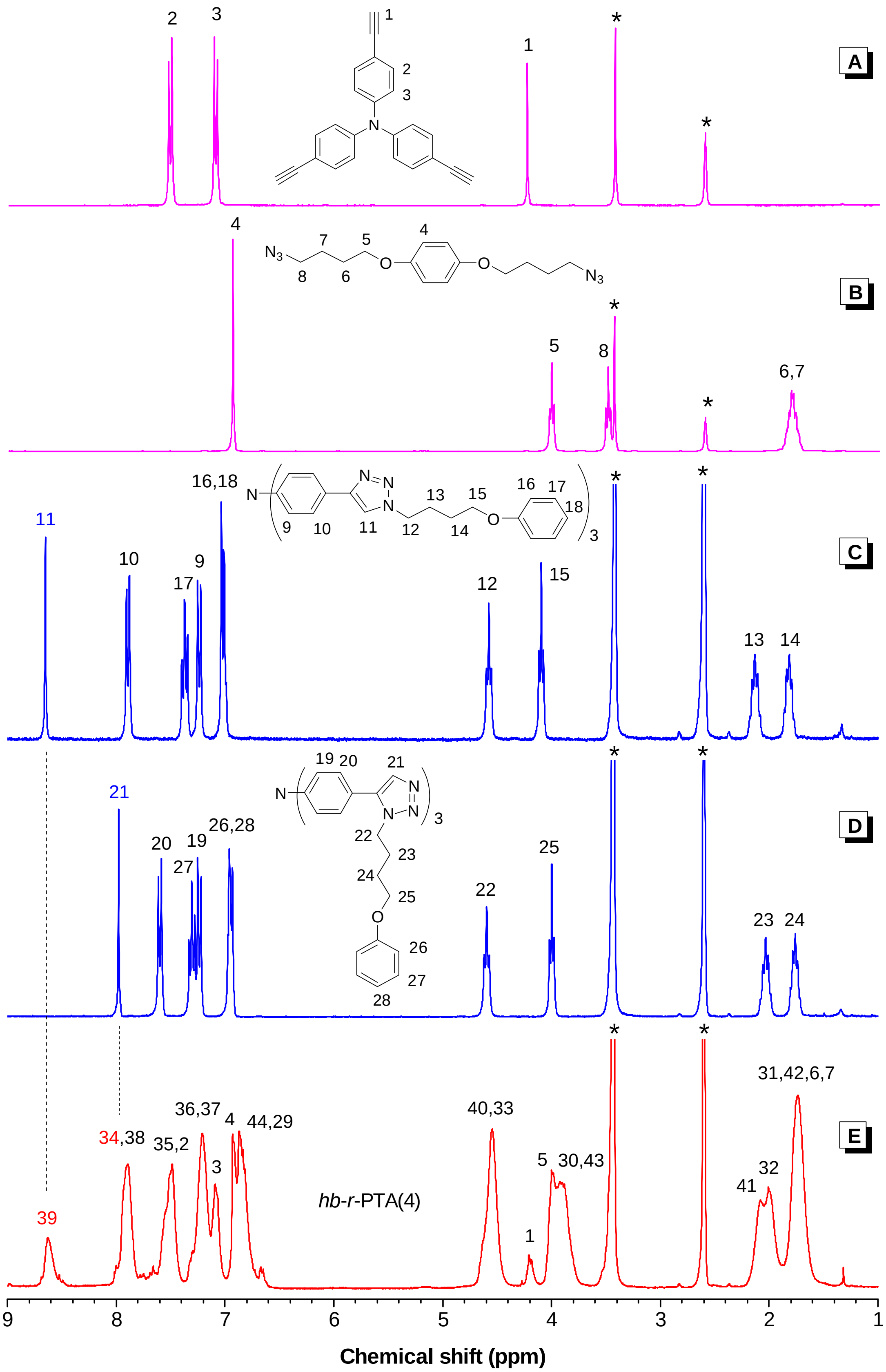
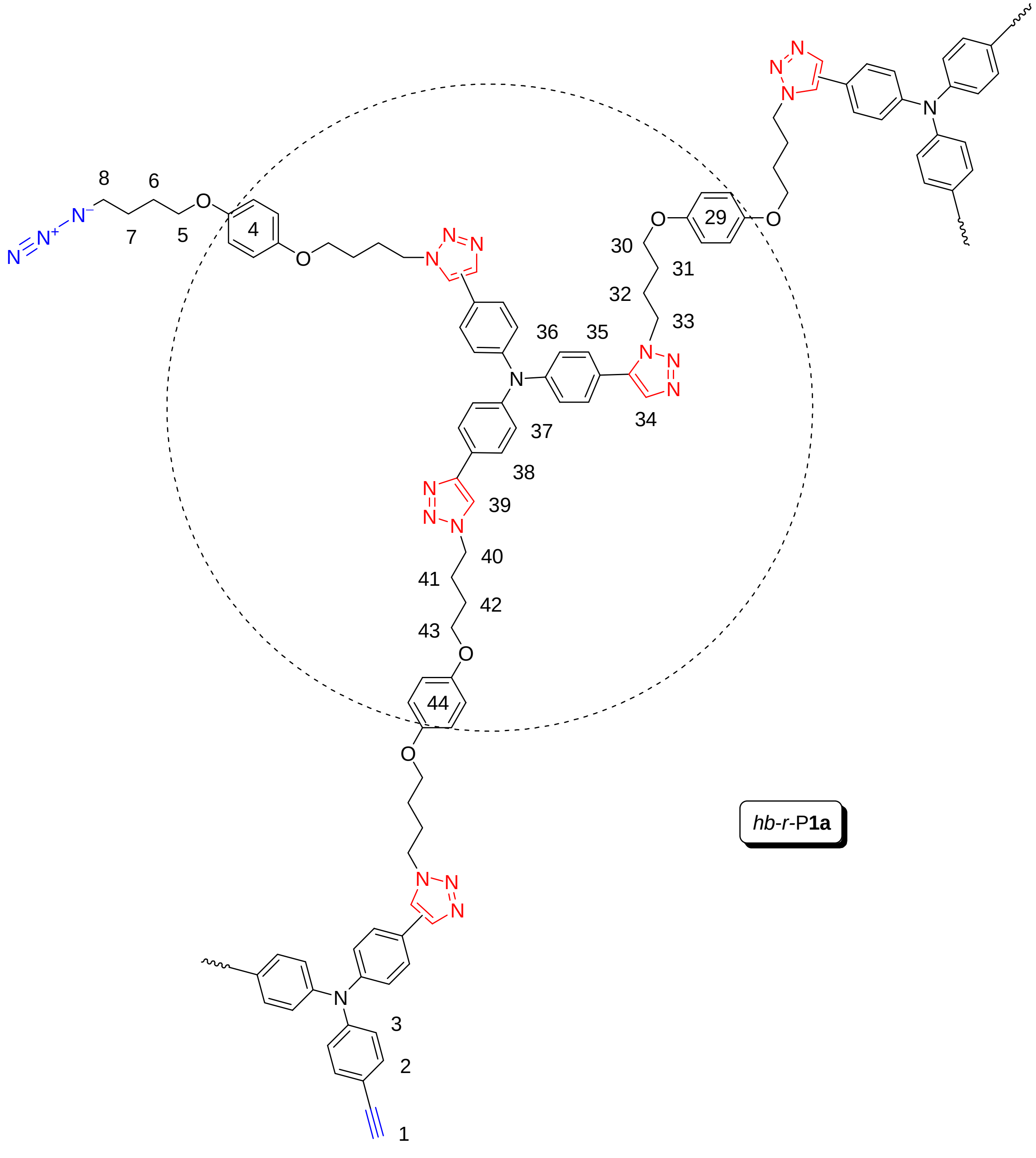


Figure S2. ^{1}H NMR spectra of monomers **3** (A) and **2a** (B), model compounds **9a** (C) and **10a** (D), and polymer *hb*-*r*-P**1a** (E) measured in DMSO-d_6 at room temperature. Labels of the resonance peaks of *hb*-*r*-P**1a** correspond to those given in Chart S1. The solvent and water peaks are marked with asterisks.

Chart S1. Chemical Structure of *hb*-*r*-P**1a** with Labeling Scheme for Spectral Analysis



hb-*r*-P**1a**

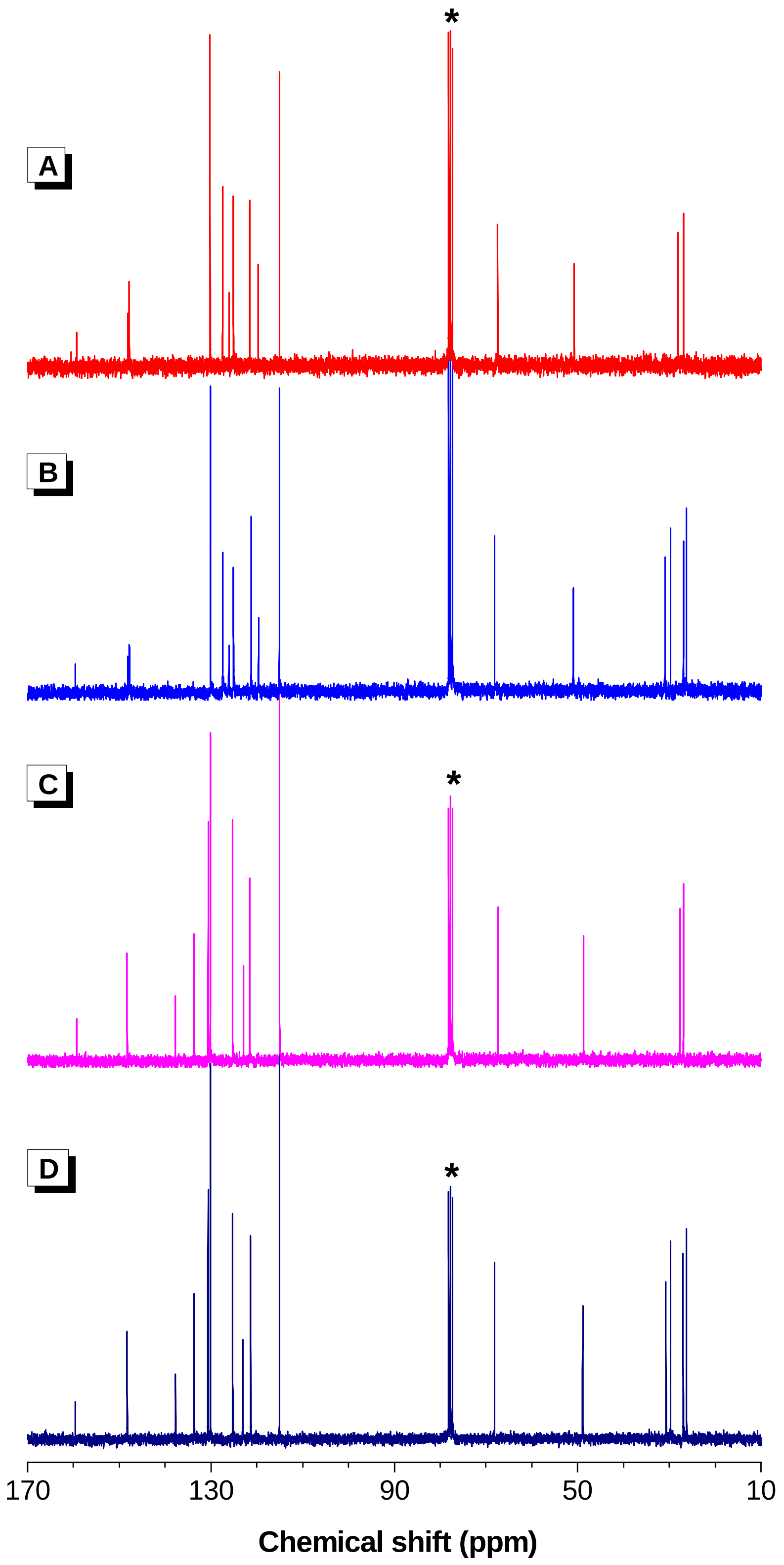


Figure S3. ^{13}C NMR spectra of model compounds **9a** (A), **9b** (B), **10a** (C) and **10b** (D) measured in chloroform-*d* at room temperature.

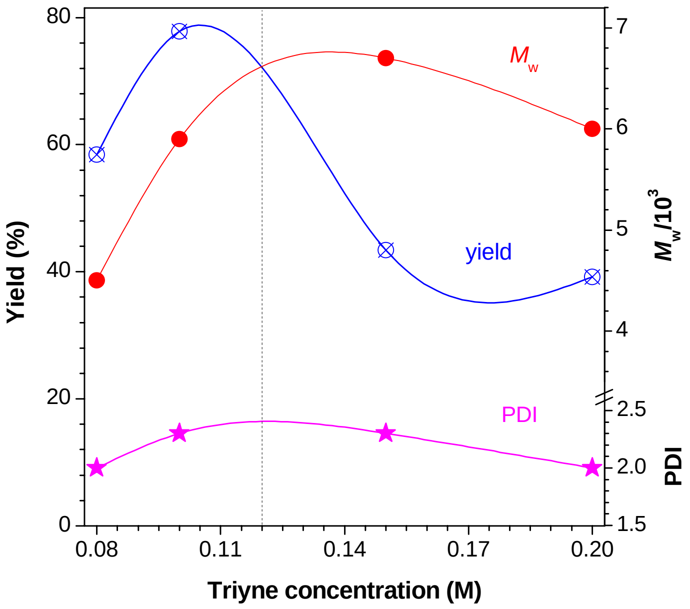


Figure S4. Effect of concentration of triyne **3** on the thermally initiated 1,3-dipolar polycycloaddition of **2a** and **3** carried out in dioxane at refluxing temperature under nitrogen for 72 h; $[\mathbf{3}]_0/[\mathbf{2a}]_0$ = 2:3.

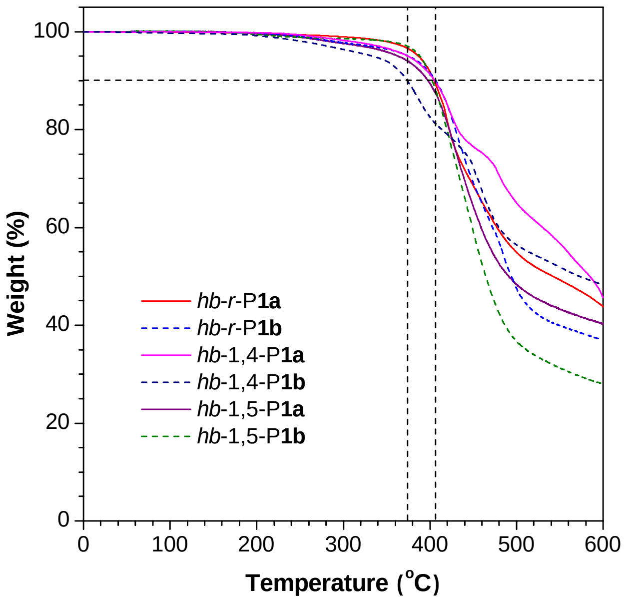


Figure S5. TGA thermographs of *hb*-PTAs recorded under nitrogen at a heating rate of 20 °C/min.

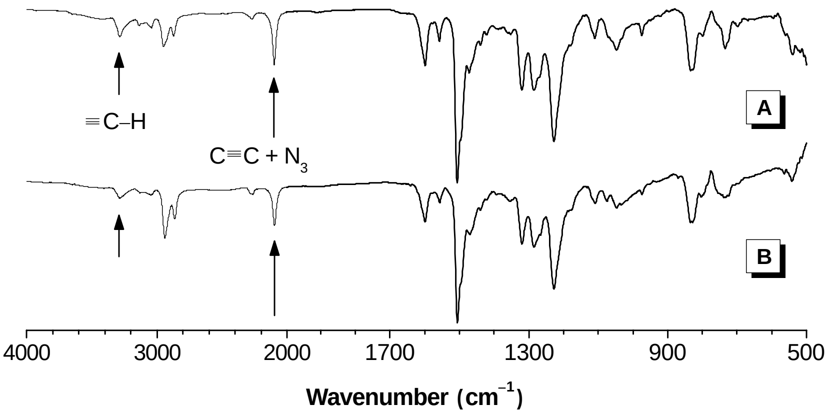


Figure S6. IR spectrum of (A) *hb*-1,4-P**1a** and (B) *hb*-1,4-P**1b**.

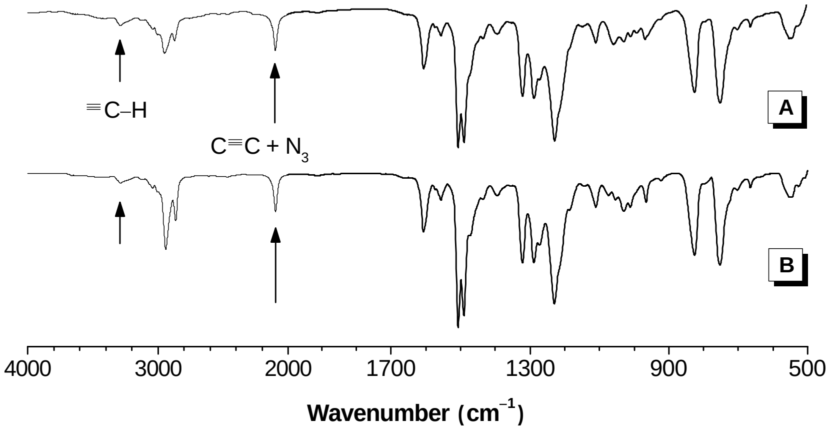


Figure S7. IR spectrum of (A) *hb*-1,5-P**1a** and (B) *hb*-1,5-P**1b**.

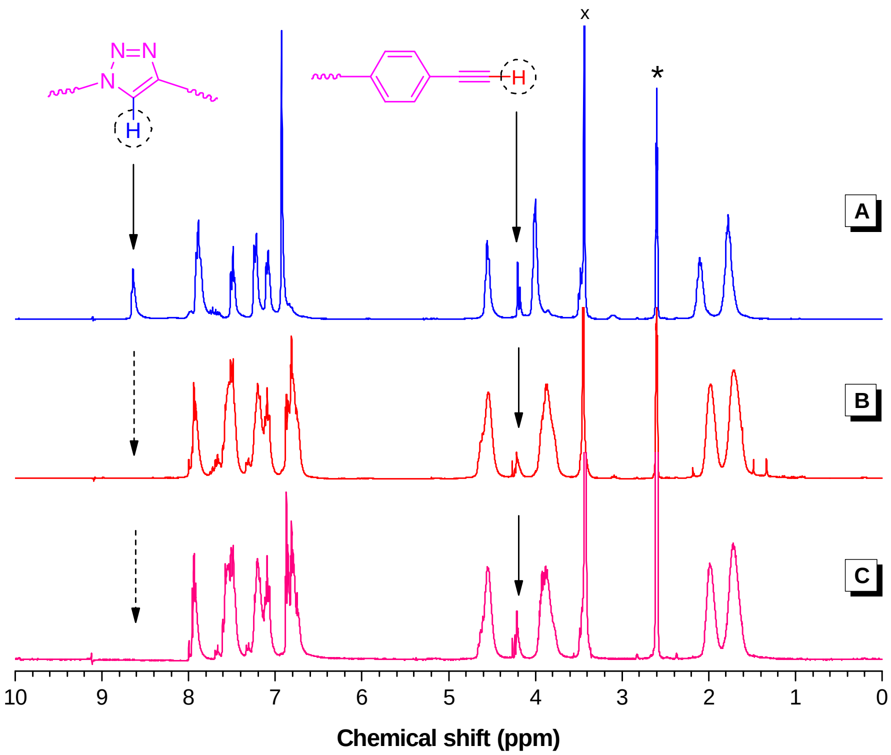


Figure S8. ^{1}H NMR spectra of (A) *hb*-1,4-P**1a** and (B and C) *hb*-1,5-P**1a** measured in DMSO-d_6 at room temperature. The peaks of water and solvent are marked with cross and asterisk, respectively. The polymers were prepared by the click polymerizations of **2a** and **3** catalyzed by (A) $Cu(PPh_3)_3Br$, (B) $Cp^*Ru(PPh_3)_2Cl$, and (C) $[Cp^*RuCl_2]_n$.

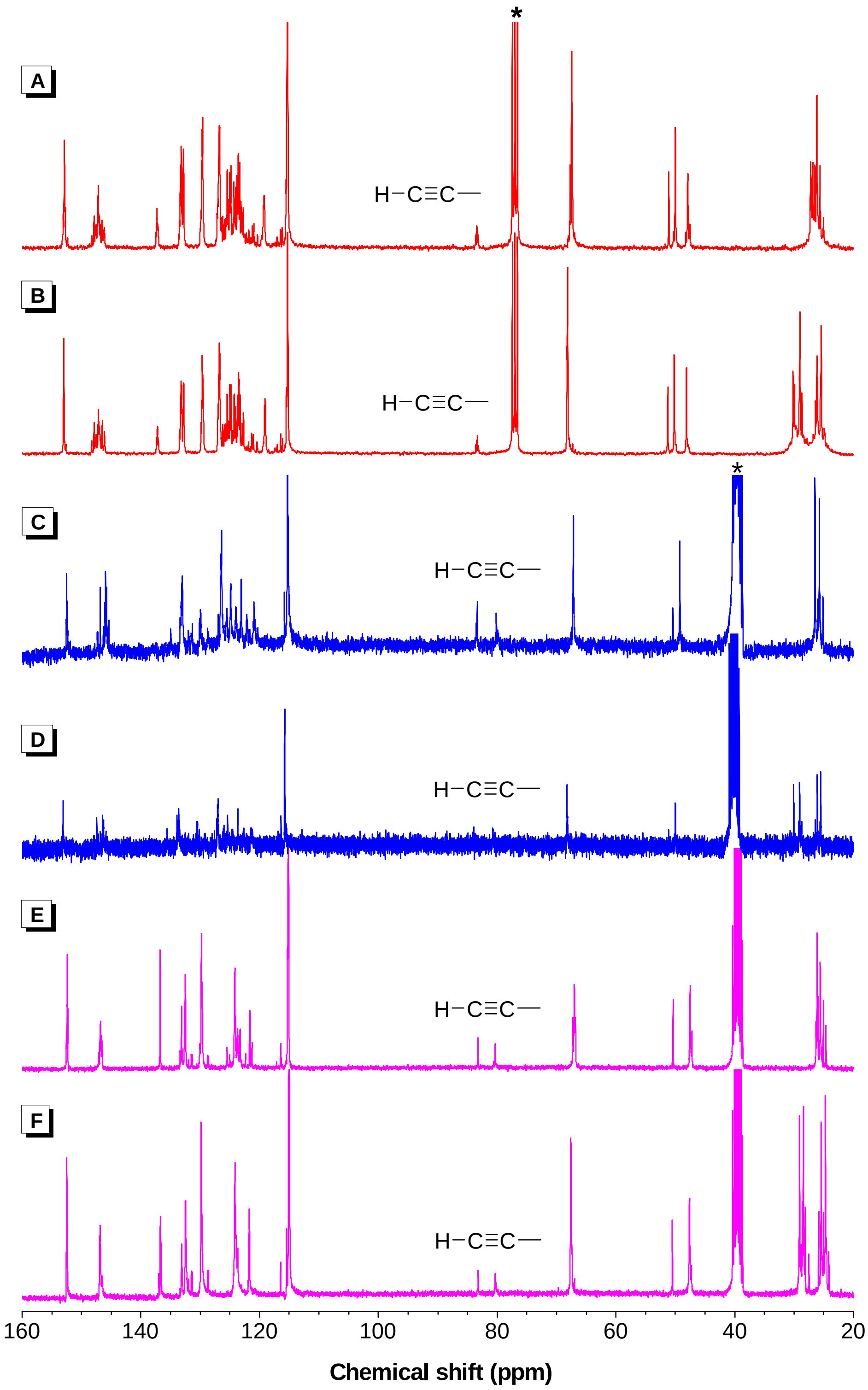


Figure S9. ^{13}C NMR spectra of *hb*-*r*-P**1a** (A) and *hb*-*r*-P**1b** (B) in chloroform-*d*, *hb*-1,4-P**1a** (C) and *hb*-1,4-P**1b** (D) in DMSO-d_6, and *hb*-1,5-P**1a** (E) and *hb*-1,5-P**1b** (F) in DMSO-d_6 measured at room temperature. The solvent peaks are marked by asterisks.

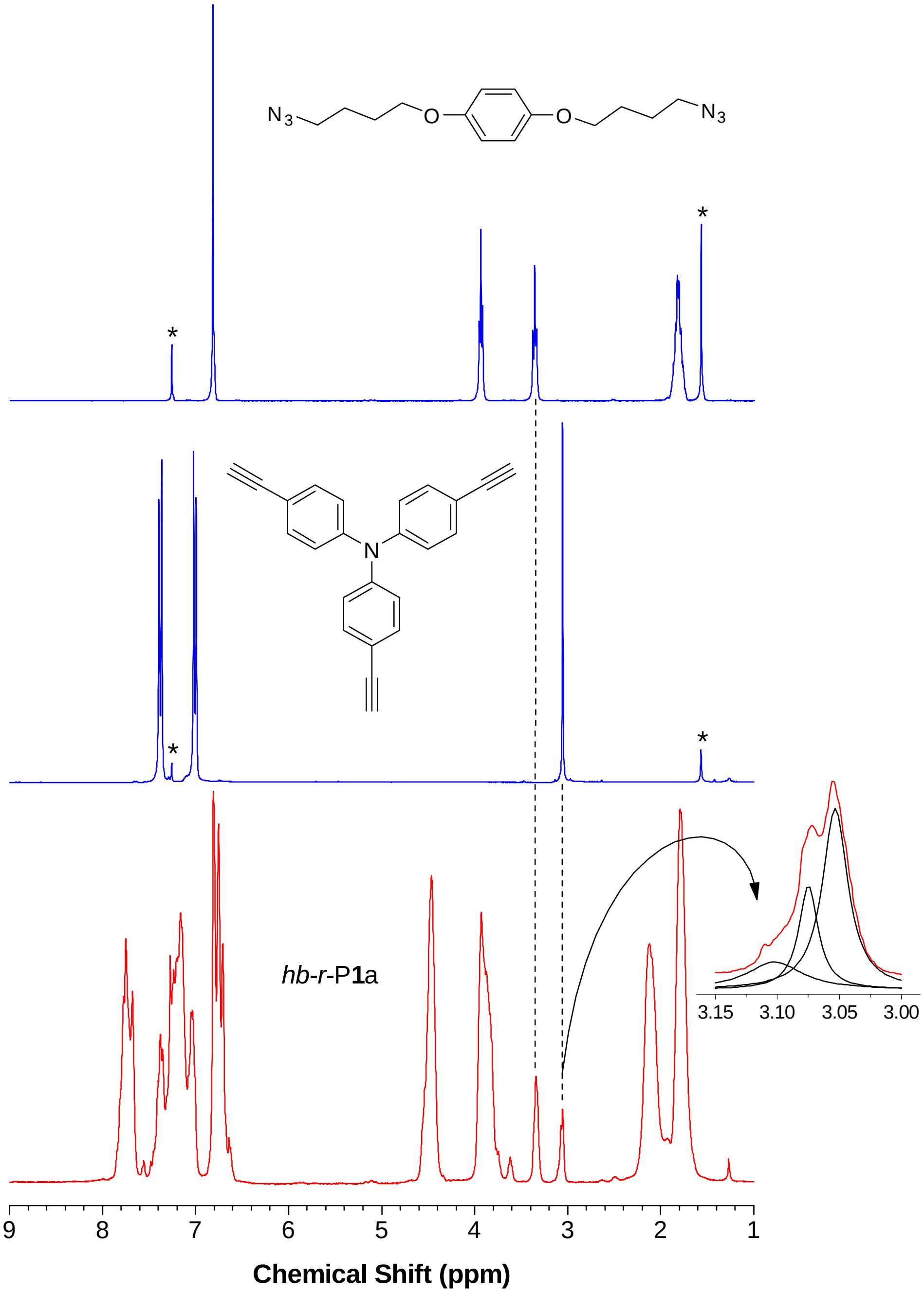


Figure S10. ^{1}H NMR spectra of chloroform-*d* solutions of monomers **3** (A) and **2a** (B) and their polymer *hb*-*r*-P**1a** (C) measured at room temperature. The solvent and water peaks are marked with asterisks.

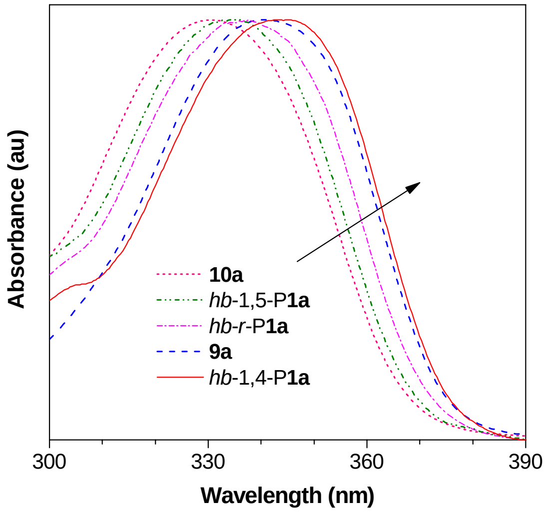


Figure S11. Normalized absorption spectra of DCM solutions of polymers *hb*-1,4-P**1a**, *hb*-*r*-P**1a** and *hb*-1,5-P**1a** and model compounds **9a** and **10a**. Solution concentrations: ~1.5 µg/mL (for polymer) and ~1 µM (for model compound).

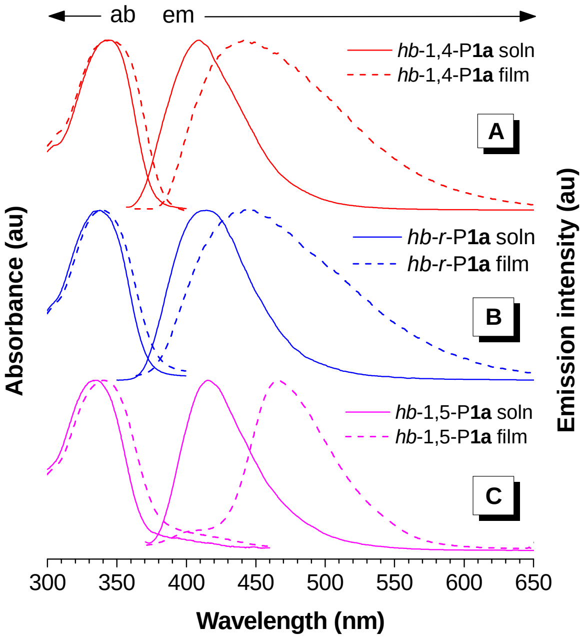


Figure S12. Normalized absorption (ab) and emission (em) spectra of DCM solutions (~1.5 µg/mL) and solid films of *hb*-PTAs. Excitation wavelength (nm): (A) *hb*-1,4-P**1a**: 345 (soln), 344 (film); (B) *hb*-*r*-P**1a**: 337 (soln), 340 (film); (C) *hb*-1,5-P**1a**: 336 (soln), 346 (film).