

Electronic Supplementary Information

Synthesis of 1,5-regioregular polytriazoles by efficient NMe₄OH-mediated azide-alkyne click polymerization

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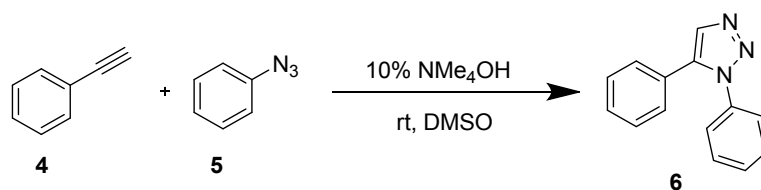
Experimental Section

General Information

The ^1H and ^{13}C NMR spectra were recorded on a Bruker ADVANCE2B 300 or 500 NMR spectrometer in $\text{DMSO-}d_6$ using tetramethylsilane (TMS; $\delta = 0$) as internal reference. The FT-IR spectra were measured on a Bruker Vector 22 spectrometer as thin films on KBr disks. The MALDI-TOF mass spectra were conducted on a GCT premier CAB048 mass spectrometer. Thermo-gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer TGA 7 under dry nitrogen at $10^\circ\text{C}/\text{min}$. The relative weight-average (M_w) and number-average (M_n) molecular weights of the polymers and their polydispersity indices (PDI, M_w/M_n) were estimated by a Waters 1515 gel permeation chromatography (GPC) system equipped with interferometric refractometer detector, using monodisperse polystyrene as calibration standards and DMF containing 0.05 M LiBr as the eluent at a flow rate of 1.0 mL/min. Tetramethylammonium hydroxide (NMe_4OH) (25 wt% solution in water), $\text{Cu}(\text{PPh}_3)\text{NO}_3$, phenylacetylene **4**, azidobenzene **5**, 1,4-diethnylbenzene (**2b**), 1,3-diethnylbenzene (**2c**) were purchased from Aldrich.

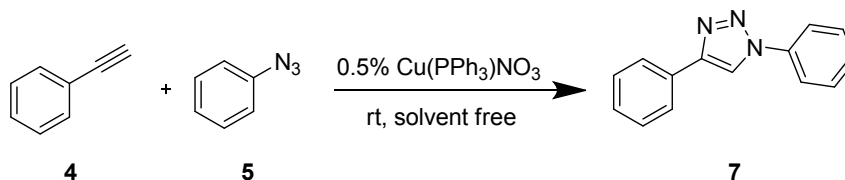
Model reaction

Preparation of 1,5-disubstituted 1,2,3-triazole derivative 6. To a DMSO solution (3.5 mL) of phenylacetylene **4** (102 mg, 1 mmol) and azidobenzene **5** (119 mg, 1.00 mmol) was added tetramethylammonium hydroxide (0.01 mmol, 25 wt% solution in water). The reaction mixture was stirred at room temperature under N_2 for 24 h. After diluted by water, the desired products were isolated by vacuum filtration, washed with water, air-dried for 1 h and then dried in vacuum overnight. Pale yellow solid (191 mg, 86%) was obtained. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, TMS): $\delta = 8.13$ (s, 1H), 7.57-7.51 (m, 3H), 7.44-7.37 (m, 5H), 7.30-7.25 (m, 2H).



Preparation of 1,4-disubstituted 1,2,3-triazole derivative 7. A 10 mL oven-dried Schlenk tube was charged with $\text{Cu}(\text{PPh}_3)\text{NO}_3$, **4** (102 mg, 1 mmol) and azidobenzene

5 (119 mg, 1.00 mmol). The mixture was stirred at room temperature for 20 min. The crude product was purified by column chromatography on silica gel to obtain the **7** in 75% yield (165 mg) as white solid. ¹H NMR (300 MHz, DMSO-*d*₆, TMS): δ = 9.31 (s, 1H), 7.98-7.94 (m, 4H), 7.67-7.62 (m, 2H), 7.54-7.49 (m, 3H), 7.41-7.37 (m, 1H).



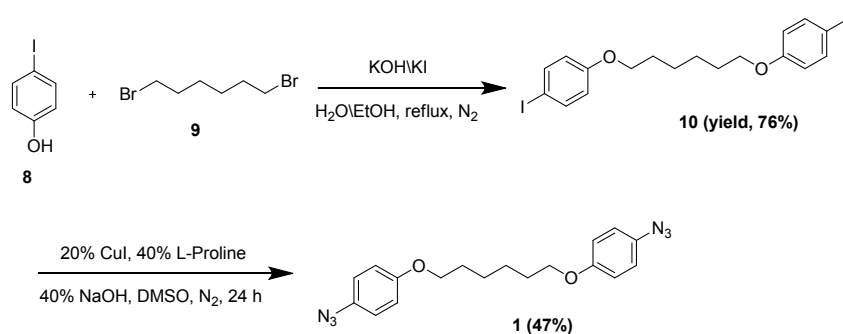
Monomer Preparation

4,4'-(Isopropylidenediphenyl)-bis(4-ethynylbenzyl) ether **2a**, 1,6-bis(4-ethynylphenoxy)hexane **2d**, 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene **2e** were prepared according to our previous publications.^{1,2}

1,6-bis(4-azidophenoxy)hexane 1. Into a 250 mL round-bottom flask were added 4-iodophenol (4.4 g, 20 mmol), NaOH (0.80 g, 20 mmol), KI (199 mg, 1.2 mmol), 20 mL water and 120 mL EtOH. 1,6-Dibromohexane (2.44g, 10 mmol) was added dropwise under the protection of N₂ by reflux. The mixture was stirred for 24 h. After cool down to room temperature and the solvent was evaporated, the residue was dissolved with dichloromethane (DCM) and washed with water for three times and dried over anhydrous MgSO₄. After filtration and removal of solvent in vacuum, the residue was purified by column chromatography on silica gel using hexane/EA (50:1) as eluent. White solid **10** (3.957g, 76%) was obtained.

Then **10** (2.61 g, 5 mmol), CuI (190 mg, 1 mmol), *L*-proline (230 mg, 2 mmol), NaN₃ (1.3 g, 20 mmol), and NaOH (80 mg, 2 mmol) in dry DMSO (20 mL) were stirred at 80 °C for 24 h under nitrogen. Afterward, the mixture was cooled down to room temperature, diluted with 100 mL DCM and washed with water. The organic phase was dried over MgSO₄. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (n-hexane: DCM = 5:1 (v/v)) to give **1** (0.827 mg, 47%) as a yellow solid. IR (thin film), ν (cm⁻¹): 2943, 2122 (N₃), 1506, 1284, 1243, 839. ¹H NMR (300 MHz, DMSO-

d_6), δ (TMS, ppm): 7.07-6.93 (m, 8H, Ar-H), 3.95 (t, 4H, $J = 6.0$ Hz, OCH₂), 1.79-1.64 (m, 4H, CH₂), 1.5-1.42 (m, 4H, CH₂). ¹³C NMR (125 MHz, DMSO- d_6), δ (ppm): 156.2, 131.3, 120.2, 115.9, 67.7, 28.6, 25.2. HRMS (MALDI-TOF): m/z 352.1652 [M^+ , calcd 352.1648].



Polymer Synthesis

Unless otherwise stated, all the polymerizations of diazide **1** and diynes **2** were carried out under nitrogen using a standard Schlenk technique. Typical experimental procedures for the click polymerization of **1** with **2a** are described below.

Into a 10 mL Schlenk tube was placed **1** (35.2 mg, 0.1 mmol) and **2a** (45.6 mg, 0.1 mmol), after evacuated and refilled with nitrogen for three times, NMe₄OH (40 μ L, 0.1 mmol, 25 wt% solution in water) and dry DMSO (2 mL) were added via syringe. The solution was stirred at room temperature for 24 h. Afterward, the resulting solution was diluted with CHCl₃ (50 mL) and washed with brine (50 mL) for three times. The organic phase was concentrated by a rotary evaporator under reduced pressure. The residue was diluted with CHCl₃ (10 mL) and added dropwise into 200 mL of hexane via a cotton filter under rigidly stirring. The precipitate was allowed to stand overnight and then collected by filtration. The polymer was washed with hexane for several times and dried under vacuum at room temperature to a constant weight.

Characterization Data for P3a. Yellow powder; yield: 86%. M_w 44 000; M_w/M_n 1.41 (GPC, determined in DMF containing 0.05 M LiBr on the basis of polystyrene calibration). IR (thin film), ν (cm⁻¹): 2939, 2122, 1514, 1249, 1180, 832. ¹H NMR (300 MHz, DMSO- d_6), δ (TMS, ppm): 9.16 (1,4-disubstituted triazoles), 8.08 (1,5-disubstituted triazoles), 7.48-6.76 (m, Ar-H), 5.01 (CH₂), 3.98 (CH₂), 1.82-1.34 (CH₂).

^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 159.2, 142.9, 132.9, 129.0, 128.4, 127.9, 127.4, 127.1, 115.1, 114.1, 68.6, 67.8, 30.6, 28.5, 25.2.

P3b. Yellow powder; yield: 91%. M_w 56 000; M_w/M_n 1.62 (GPC, determined in DMF containing 0.05 M LiBr on the basis of polystyrene calibration). IR (thin film), ν (cm^{-1}): 2938, 2122, 1514, 1251, 990, 834. ^1H NMR (300 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 8.11 (1,5-disubstituted triazoles), 7.35-6.92 (m, Ar-H), 3.98 (CH_2), 1.90-1.20 (CH_2). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 159.3, 136.7, 133.1, 129.1, 127.1, 115.0, 67.8, 28.6, 25.3.

P3c. Yellow powder; yield: 96%. M_w 41 000; M_w/M_n 1.33 (GPC, determined in DMF containing 0.05 M LiBr on the basis of polystyrene calibration). IR (thin film), ν (cm^{-1}): 2938, 2105, 1515, 1251, 1172, 835. ^1H NMR (300 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 7.97 (1,5-disubstituted triazoles), 7.44-6.93 (m, Ar-H), 4.00 (CH_2), 1.91-1.30 (CH_2). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 159.3, 136.8, 133.0, 129.3, 128.8, 128.7, 127.1, 115.1, 67.8, 28.5, 25.2.

P3d. Yellow powder; yield: 89%. M_w 17 000; M_w/M_n 1.22 (GPC, determined in DMF containing 0.05 M LiBr on the basis of polystyrene calibration). IR (thin film), ν (cm^{-1}): 2938, 1605, 1510, 1254, 840. ^1H NMR (300 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 7.99 (1,5-disubstituted triazoles), 7.51-6.75 (m, Ar-H), 3.98 (CH_2), 1.86-1.21 (CH_2). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 159.1, 150.0, 142.3, 137.5, 133.2, 132.3, 131.3, 129.7, 129.1, 127.0, 118.4, 115.3, 115.0, 114.6, 83.5, 79.1, 67.5, 28.5, 25.2.

P3e. Yellow powder; yield: 85%. M_w 40 300; M_w/M_n 1.45 (GPC, determined in DMF containing 0.05 M LiBr on the basis of polystyrene calibration). IR (thin film), ν (cm^{-1}): 2935, 2105, 1515, 1250, 834, 702. ^1H NMR (300 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 8.05 (1,5-disubstituted triazoles), 7.30-6.66 (m, Ar-H), 4.11-3.65 (CH_2), 1.87-1.14 (CH_2). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 159.1, 143.5, 142.4, 140.4, 137.0, 132.8, 131.0, 130.6, 128.9, 127.9, 126.8, 124.7, 114.9, 67.8, 28.4, 25.3.

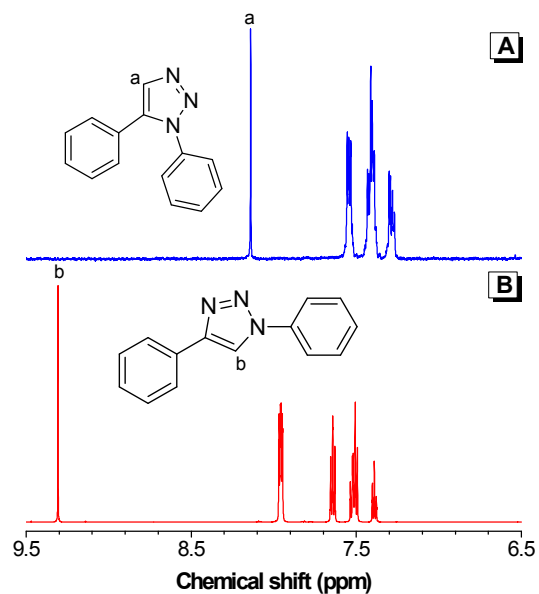


Figure S1. ^1H NMR spectra of 1,5- and 1,4-disubstituted 1,2,3-triazoles **6** (A) and **7** (B) in $\text{DMSO-}d_6$.

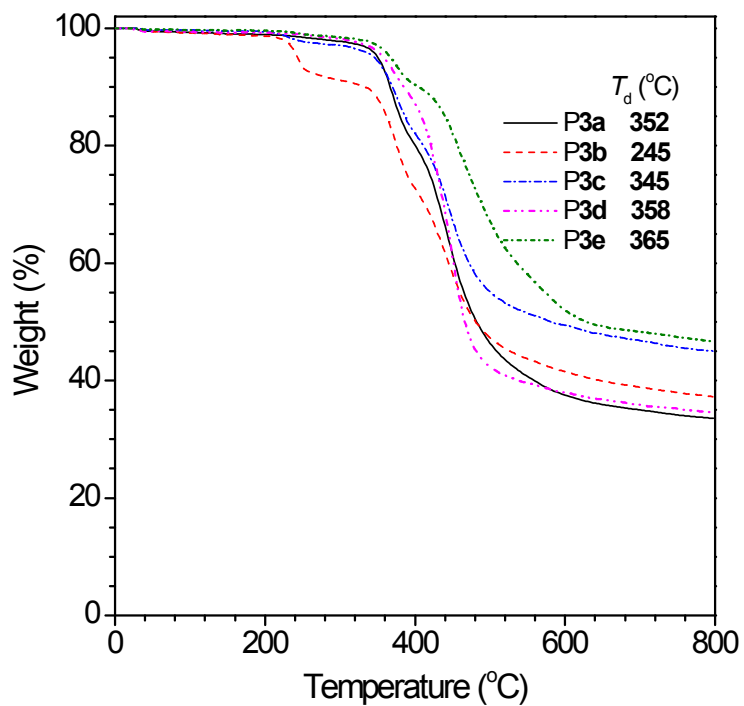


Figure S2. TGA curves of P3a-P3e recorded under nitrogen at a heating rate of $10^{\circ}\text{C}/\text{min}$.

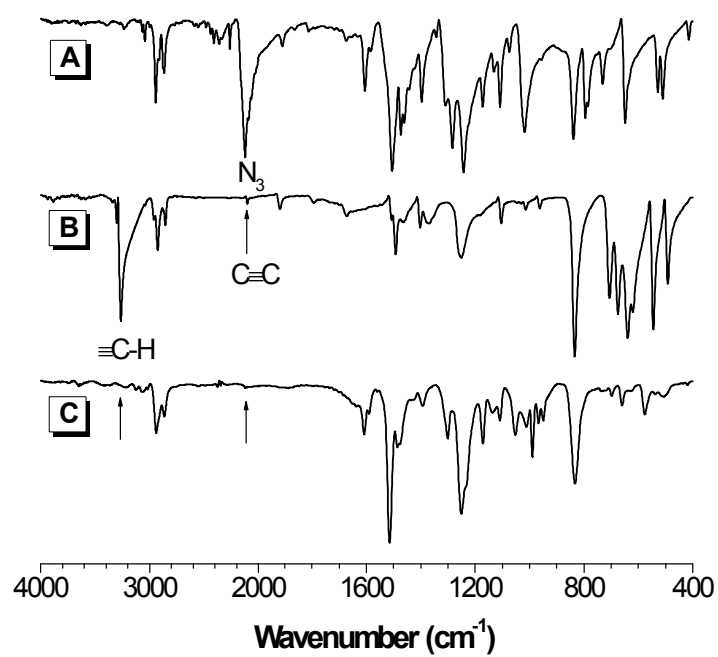


Figure S3. FT-IR spectra of monomers **1** (A) and **2b** (B) and their polymer **P3b** (C).

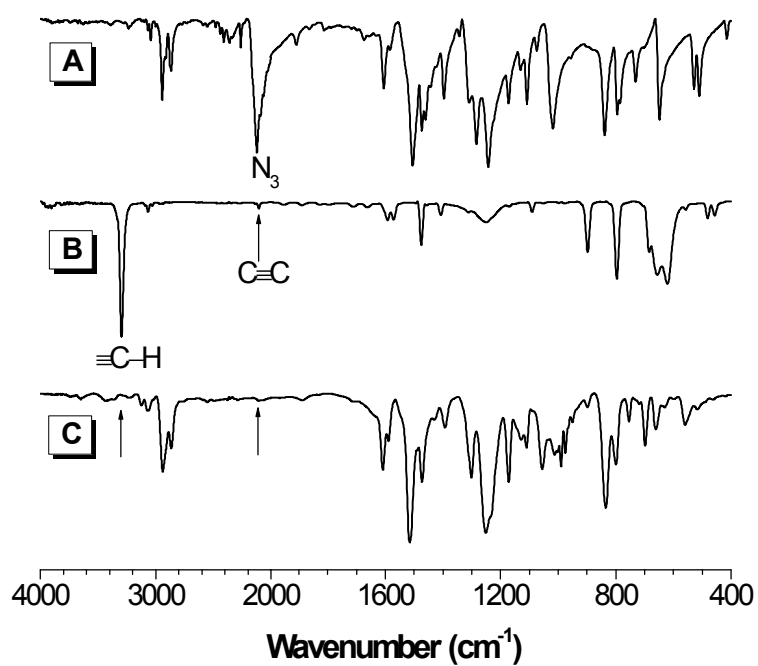


Figure S4. FT-IR spectra of monomer **1**(A) and **2c** (B) and their polymer **P3c** (C).

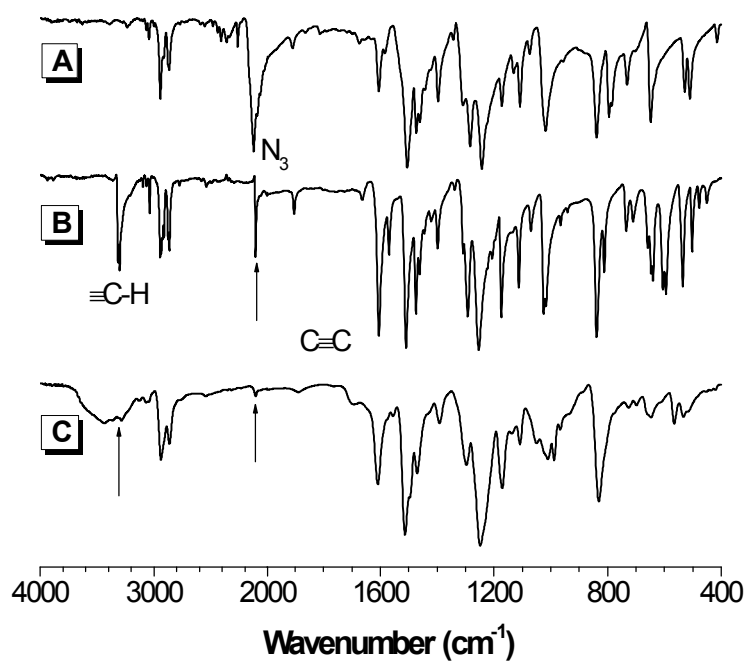


Figure S5. FT-IR spectra of monomer **1** (A) and **2d** (B) and their polymer **P3d** (C).

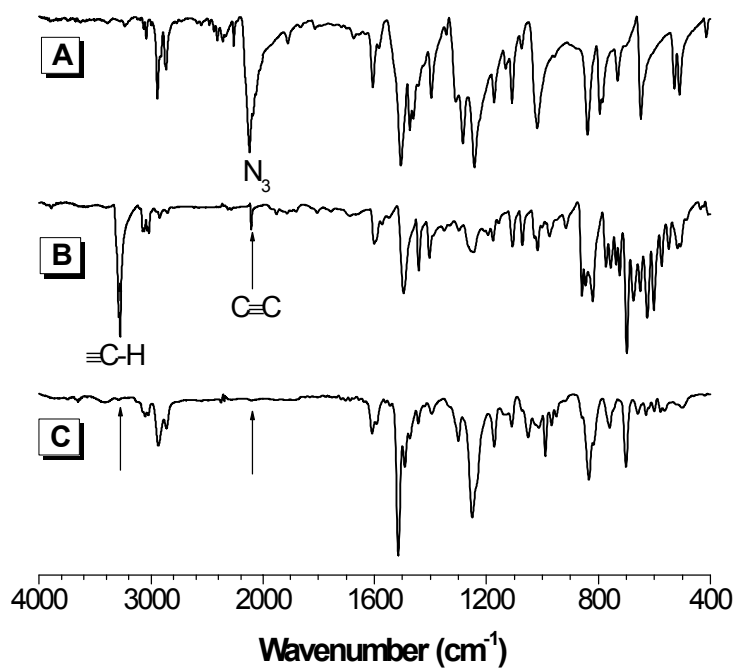


Figure S6. FT-IR spectra of monomer **1** (A) and **2e** (B) and their polymer **P3e** (C).

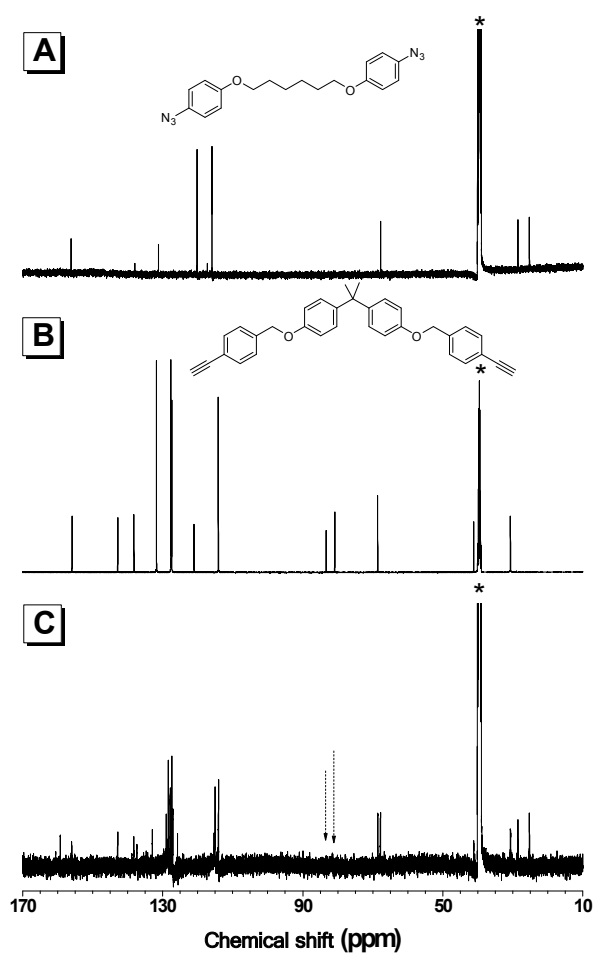


Figure S7. ^{13}C NMR spectra of monomer (A) **1** and (B) **2a** and their polymer (C) **P3a** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

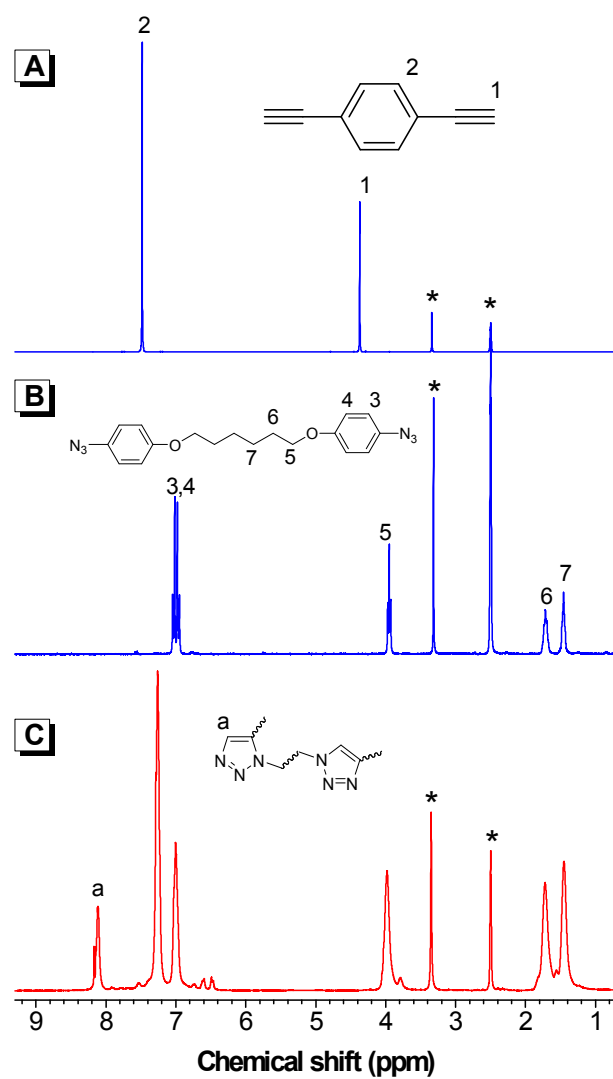


Figure S8. ^1H NMR spectra of monomer **2b** (A) and **1** (B) and their polymer **P3b** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

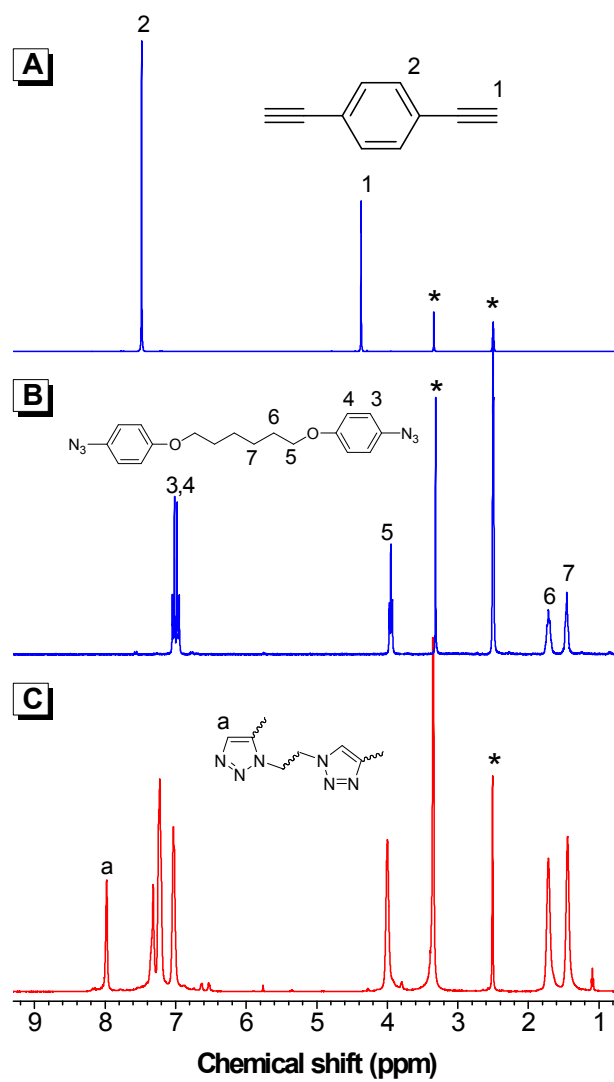


Figure S9. ^1H NMR spectra of monomer **2c** (A) and **1** (B) and their polymer **P3c** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

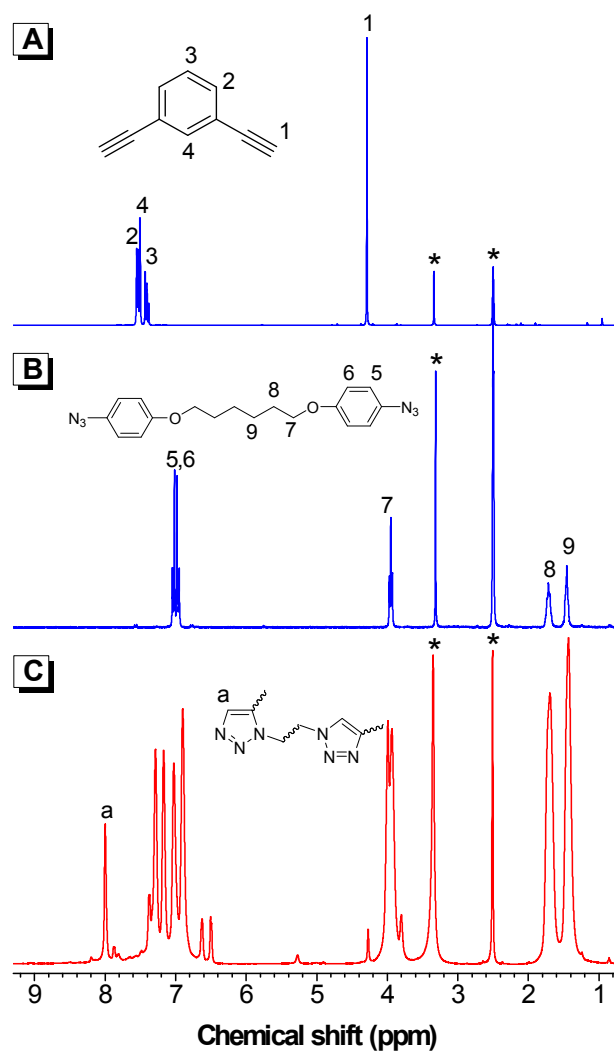


Figure S10. ^1H NMR spectra of monomer (A) **2d** and (B) **1** and their polymer (C) **P3d** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

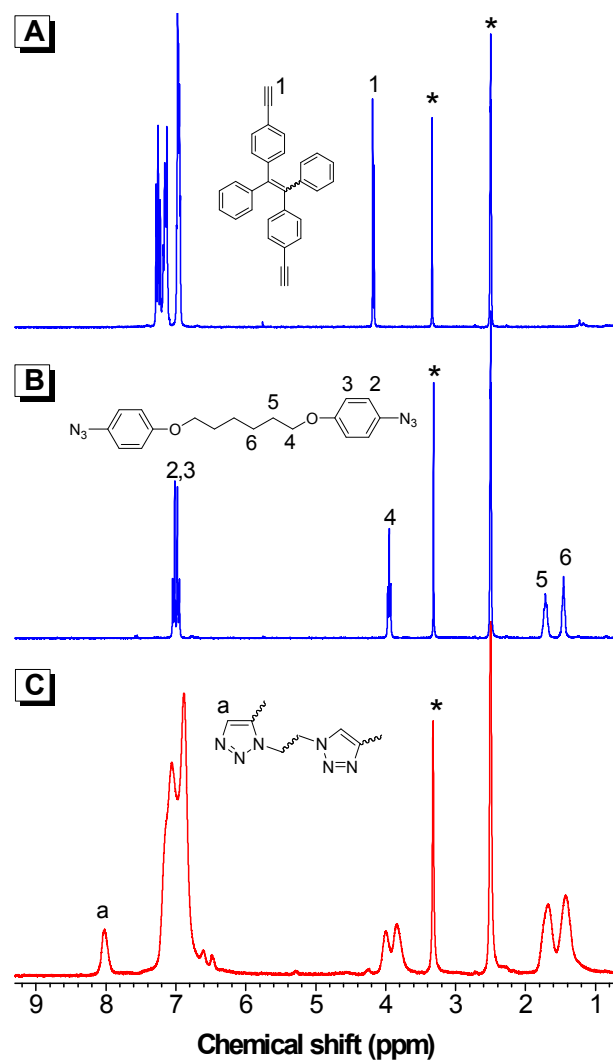


Figure S11. ^1H NMR spectra of monomer **2e** (A) and (B) **1** and their polymer **P3e** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

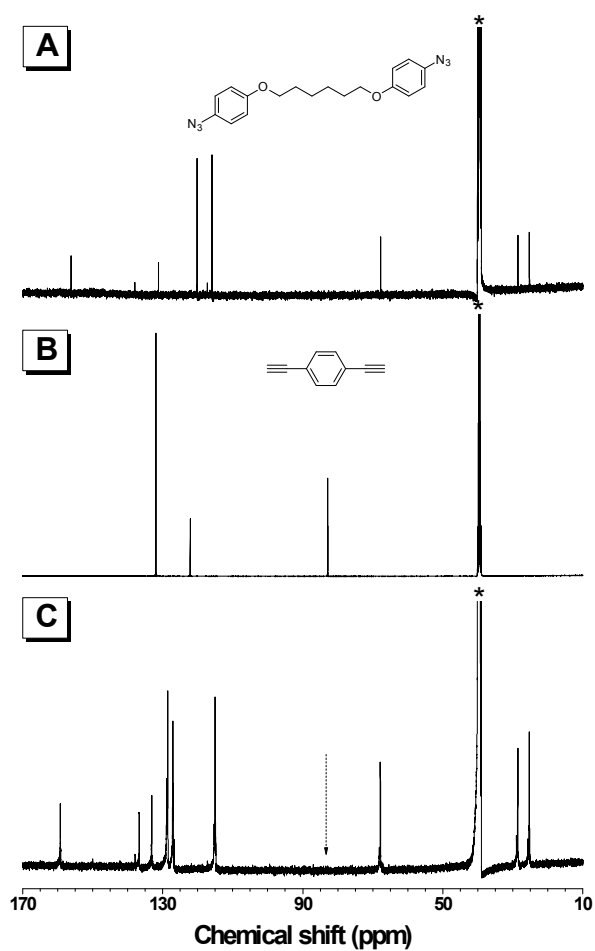


Figure S12. ^{13}C NMR spectra of monomer **1** (A) and **2b** (B) and their polymer **P3b** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

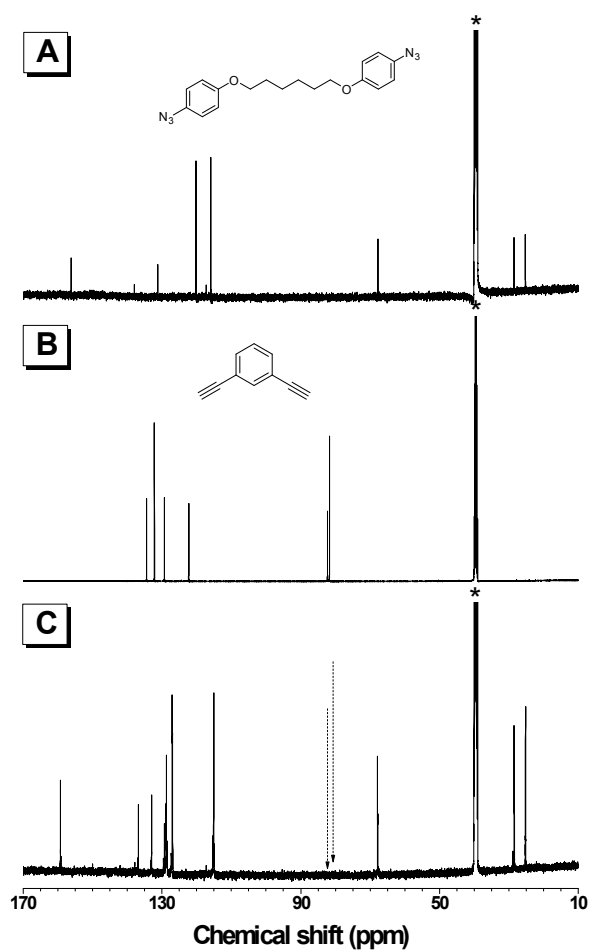


Figure S13. ^{13}C NMR spectra of monomer **1** (A) and (B) **2c** and their polymer **P3c** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

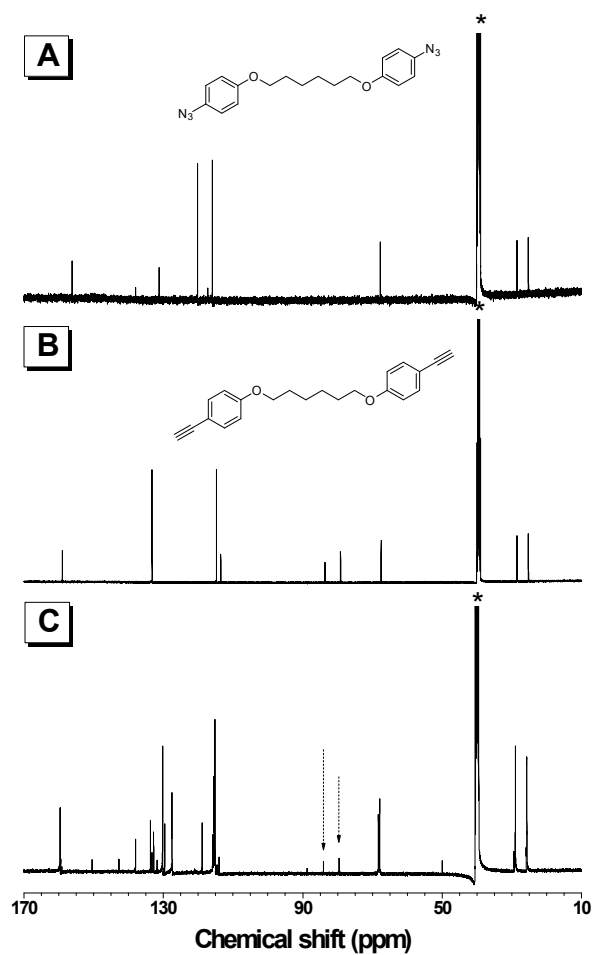


Figure S14. ^{13}C NMR spectra of monomer (A) **1** and (B) **2d** and their polymer (C) **P3d** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

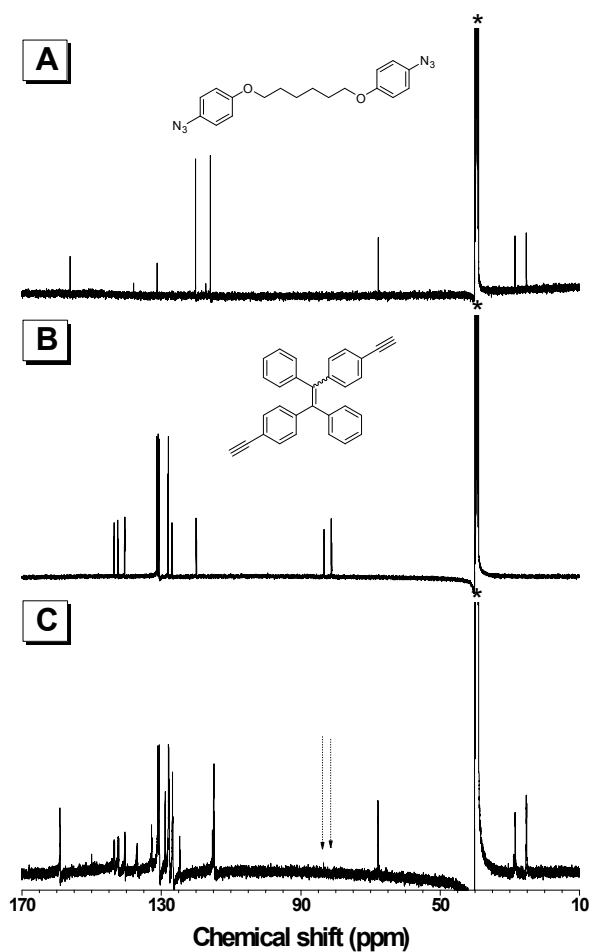


Figure S15. ^{13}C NMR spectra of monomer **1** (A) and **2e** (B) and their polymer **P3e** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

Table S1. Effect of temperature on the polymerization of **1** and **2a**.^a

| entry | T ($^{\circ}\text{C}$) | yield (%) | M_w^b | PDI^b |
|-------|----------------------------|-----------|---------|----------------|
| 1 | rt | 80 | 23 000 | 1.18 |
| 2 | 60 | 67 | 24 000 | 1.19 |
| 3 | 80 | 68 | 25 000 | 1.31 |
| 4 | 100 | 66 | 24 000 | 1.29 |

^a Polymerizations were carried out in DMSO under nitrogen for 2 h. $[\text{M}] = 0.05 \text{ M}$; $[\text{NMe}_4\text{OH}] = 0.01 \text{ M}$. ^b Estimated by gel permeation chromatography (GPC) in DMF containing 0.05 M LiBr solution on the basis of a polystyrene calibration.

Table S2. Effect of the amount of NMe₄OH on the polymerization of **1** and **2a**.^a

| entry | [NMe ₄ OH] (%) | yield (%) | <i>M</i> _w ^b | PDI |
|-------|---------------------------|-----------|------------------------------------|------|
| 1 | 40 | 79 | 31 000 | 1.30 |
| 2 | 60 | 83 | 34 000 | 1.26 |
| 3 | 80 | 72 | 33 000 | 1.18 |
| 4 | 100 | 78 | 31 000 | 1.32 |

^a Polymerizations were carried out in DMSO under nitrogen at rt for 2 h. [M] = 0.05; the amount of NMe₄OH was based on **1**. ^b Estimated by gel permeation chromatography (GPC) in DMF containing 0.05 M LiBr solution on the basis of a polystyrene calibration

Table S3. Effect of time on the polymerization of **1** and **2a**.^a

| entry | <i>t</i> (h) | yield (%) | <i>M</i> _w ^b | PDI |
|-------|--------------|-----------|------------------------------------|------|
| 1 | 12 | 86 | 36 000 | 1.33 |
| 2 | 24 | 86 | 44 000 | 1.39 |

^a Polymerizations were carried out in DMSO under nitrogen at rt. [M] = 0.05; [NMe₄OH] = 0.05. ^b Estimated by gel permeation chromatography (GPC) in DMF containing 0.05 M LiBr solution on the basis of a polystyrene calibration

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1. Z. Wang, Y. Shi, J. Wang, L. Z. Li, H. Q. Wu, B. C. Yao, J. Z. Sun, A. J. Qin and B. Z. Tang, *Polym. Chem.* 2014, **5**, 5890.
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