

Supporting Information (SI)

Diversified synthesis of poly(sulfonyl isourea)s by multicomponent polymerizations of isocyanides, sulfonyl azides, and alcohols/phenols

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Experimental Section

Materials and Methods

Isocyanides (**1a–1d**), sulfonyl azides (**2d**), alcohols (**3a–3e**), and CoC_2O_4 were purchased from commercial suppliers including Bidepharm, Macklin, Adamas, Energy and Aladdin they were used as received without further purification. Solvents such as dichloroethane (DCE), tetrahydrofuran (THF), acetonitrile (MeCN), toluene and *N,N*-dimethylformamide (DMF) used for the polymerization reactions were ultra-dry reagents with molecular sieves and were purchased from J&K Scientific. Isocyanide **1e–1f**, disulfonyl azides **2a–2c**, were prepared according to the previously reported procedures.^{1,2}

^1H and ^{13}C NMR spectra of monomers, model compound, and polymers were measured on a Bruker AVANCE III 600, 500 or 400 MHz NMR spectrometer at 298 K. Chemical shifts were calibrated using CDCl_3 (^1H NMR: δ 7.26 ppm; ^{13}C NMR: δ 77.16 ppm) as internal reference. High-resolution mass spectra (HRMS) were measured on a Xevo G2-XS Qtof mass spectrometer in the electrospray ionization (ESI) mode. FT-IR spectra were determined on a Nicolet 6700 FTIR spectrophotometer. Relative weight-average molecular weights (M_w), number-average molecular weights (M_n), and polydispersity indices (D , M_w/M_n) of the obtained polymers were estimated by Waters ACQUITY advanced polymer chromatography system using reactive index (RI) detector and calibrated using a set of monodispersed polystyrene standards. DMF/LiBr solution (0.05 M LiBr) was used as eluent at a flow rate of 0.5 mL/min. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurement was carried out on a TA TGA 55 and a TA DSC Q200 instrument, respectively, under nitrogen at a heating rate of 10 °C/min.

Synthesis and Characterization

Model reaction

model-1 was synthesized according to reported procedures in literature.³ The detailed synthetic procedures were provided as follows. To the stirring mixture of isonitriles **1a** (0.6 mmol), sulfonyl azides **2d** (0.5 mmol), ethyl alcohol **3d** (2 mL), and CoC_2O_4 (5 mol%) was added DCE (2 mL). The whole reaction mixture was stirred for 12 h at room temperature. Evaporation of the solvent followed by purification on a silica gel column (eluent: PE/EA = 4/1) as eluents to afford pure product as white solid. IR (neat), ν (cm^{-1}): 3310, 2921, 1730, 1593, 1421, 1280, 1135, 1078, 943, 813, 673, 559, 462. ^1H NMR (600 MHz, CDCl_3), δ (ppm): 8.09 (t, $J = 6$ Hz, 1H), 7.81 (d, $J = 6$ Hz, 2H), 7.61 (d, $J = 6$ Hz, 2H), 7.33 (d, $J = 6$ Hz, 2H), 7.23 (d, $J = 6$ Hz, 2H), 4.54 (d, $J = 6$ Hz, 2H), 3.91 (q, $J = 6$ Hz, 2H), 2.45 (s, 3H), 2.41 (s, 3H), 0.97 (t, $J = 6$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3), δ (ppm): 155.99, 145.62, 143.23, 139.15, 133.55, 129.99, 129.42, 128.95, 126.36, 65.44, 61.80, 21.64, 21.54, 13.59. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. 411.1043 for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_5\text{S}_2$, found 411.1068.

Synthesis of Polymers

The synthetic procedure to **P1a2a3a** (Table 1, entry 12) was given below as an example. To a 10 mL Schlenk tube were sequentially added isonitriles **1a** (156 mg, 0.8 mmol), sulfonyl azides **2a** (76 mg, 0.2 mmol), 1,6-hexanediol **3a** (24 mg, 0.2 mmol), and CoC_2O_4 (9 mg, 30 mol%) was added MeCN (1 mL). The resulting reaction mixture was stirred at 80 °C for 24 h. Upon completion, the resulting solution was diluted with 2 mL of DCM and then added dropwise into 100 mL Et_2O through a neutral Al_2O_3 -filled dropper to remove the insoluble substances, if any. The precipitate was finally collected after filtration, being washed with Et_2O , and dried under vacuum at 60 °C to a constant weight. The structural characterization results were summarized as follows.

Characterization Data for P1a2a3a: brownish-yellow powder. 75% yield. M_n : 11800; M_w : 15300; M_w/M_n : 1.3 (GPC, polystyrene calibration). IR (neat), ν (cm^{-1}): 3297, 2942, 1700, 1596, 1484, 1284, 1238, 1137, 1080, 813, 701, 559, 509. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.75, 8.05–7.93, 7.78–7.68, 7.44–6.92, 4.63–4.44, 4.16–3.82, 2.52–2.24, 1.60–1.25. ^{13}C NMR (150 MHz, CDCl_3), δ (ppm): 159.37, 156.53, 145.87, 137.52, 133.70, 130.21, 128.85, 127.04, 119.10, 69.34, 61.90, 32.19, 26.32, 21.72.

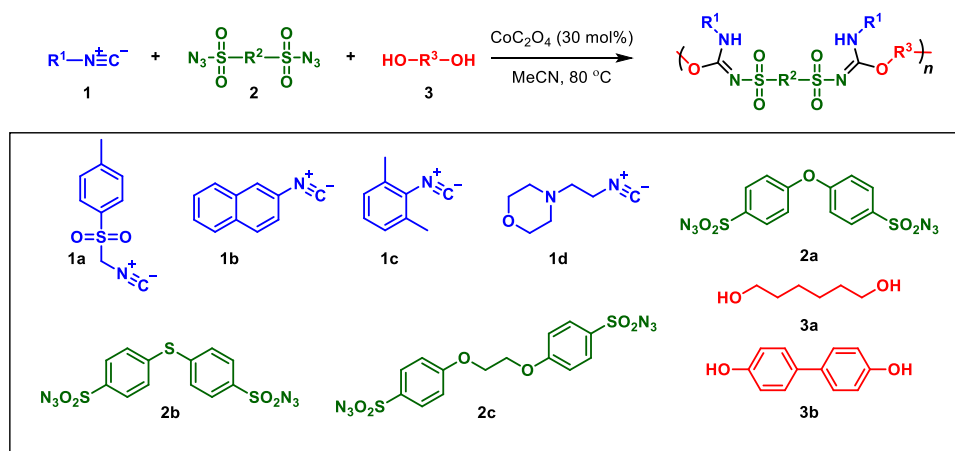
Characterization Data for P1e2d3a: tawny powder. 25% yield. M_n : 20500; M_w : 22600; M_w/M_n : 1.1 (GPC, polystyrene calibration). IR (neat), ν (cm^{-1}): 3291, 2931, 1581, 1430, 1334, 1276, 1133, 1068, 811, 673, 605, 551, 420. ^1H NMR (600 MHz, CDCl_3) δ (ppm): 8.76–8.50, 8.08–7.62, 7.43–7.16, 7.06–6.85, 4.40–3.92, 3.88–3.65, 2.60–1.87, 1.52–0.52. ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 157.35, 142.83, 141.25, 140.67, 139.84, 135.81, 130.39, 129.34, 128.64, 127.10, 126.17, 68.43, 41.10, 28.12, 24.87, 24.75, 21.48, 18.13, 14.63.

Characterization Data for P1e2a3d: yellow powder. 87% yield. M_n : 44000; M_w : 78300; M_w/M_n : 1.8 (GPC, polystyrene calibration). IR (neat), ν (cm^{-1}): 3284, 2967, 1573, 1575, 1434, 1334, 1238, 1134, 1066, 1004, 925, 856, 702, 605, 457, 414. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.65, 8.00, 7.12, 6.91, 6.89, 4.38–4.16, 3.86, 2.57–2.39, 2.12, 1.19–1.06. ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 159.16, 157.39, 141.21, 140.65, 138.33, 135.78, 130.31, 128.71, 128.56, 127.13, 118.95, 64.97, 41.10, 24.87, 18.15, 14.58, 14.22.

Characterization Data for P1f2a3d: tawny powder. 76% yield. M_n : 36300; M_w : 120500; M_w/M_n : 3.3 (GPC, polystyrene calibration). IR (neat), ν (cm^{-1}): 3293, 2977, 1604, 1573, 1481, 1430, 1234, 1137, 1064, 871, 701, 555, 405. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 9.28, 8.02–7.88, 7.21–7.05, 4.43–4.23, 3.94, 1.36–1.16. ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 159.15, 155.73, 138.28, 138.12, 133.83, 129.48, 128.51, 122.72, 118.98, 65.45, 40.60, 14.06.

Supplementary Figures

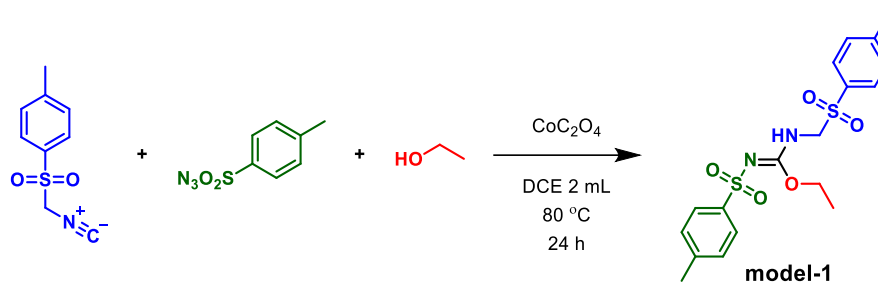
Table S1. Monomer extensions of A₁, B₂ and C₂ multicomponent polymerization.^a



entry	polymer	yield (%)	M_n^b	M_w^b	D^b
1	P1a2a3a	75	11800	15300	1.3
2	P1b2a3a	NR ^c	-	-	-
3	P1c2a3a	44 ^d	17200	19900	1.2
4	P1d2a3a	62 ^d	12500	15500	1.2
5	P1a2b3a	gel	-	-	-
6	P1a2c3a	UD ^e	-	-	-
7	P1a2a3b	47 ^f	10400	12500	1.2

^a Unless otherwise noted, the polymerizations were carried out with [2] = 0.2 mmol, CoC₂O₄ (30 mol%) in a ratio of [1]:[2]:[3] = 4:1:1 in MeCN solvent at 80 °C for 24 h under air atmosphere. ^b Estimated by gel permeation chromatography (GPC) with DMF containing 0.05 M LiBr as the mobile phase on the basis of a linear polystyrene calibration. Dispersity (D) = M_w/M_n . ^c No Reaction. ^d Product with the coexistence of desired structure and impure structure. ^e Product with undesired and unidentified structures. ^f Isomeric structure units may exist in the polymer backbone.

Scheme S1. Synthetic route to model-1.



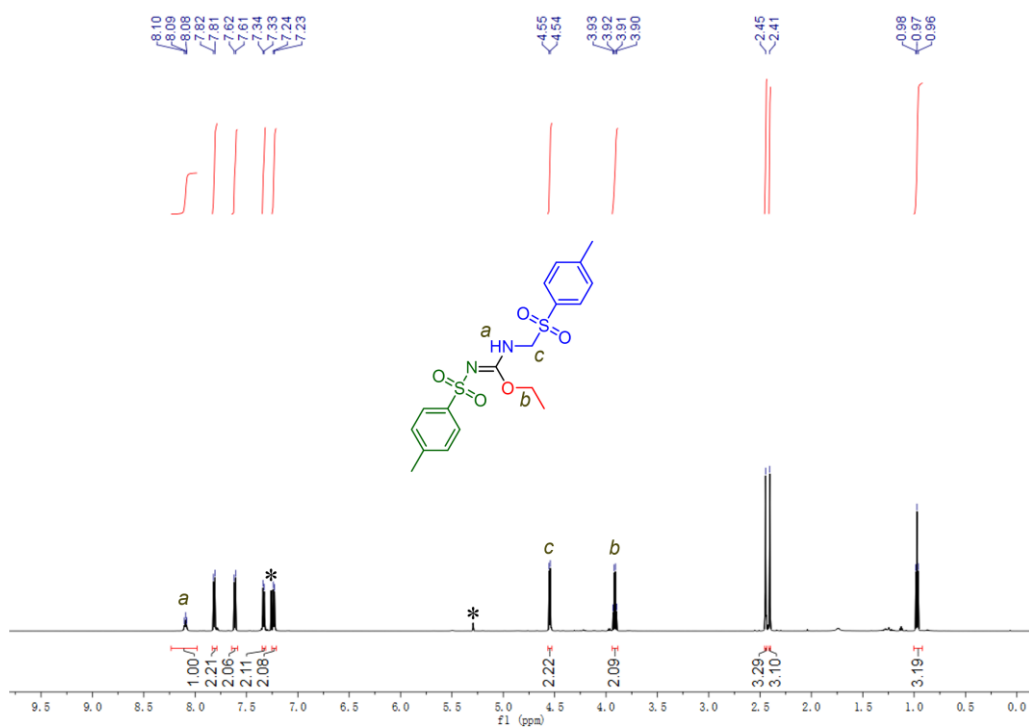


Figure S1. ^1H NMR spectrum of **model-1** in CDCl₃. The solvent peaks are marked with asterisks.

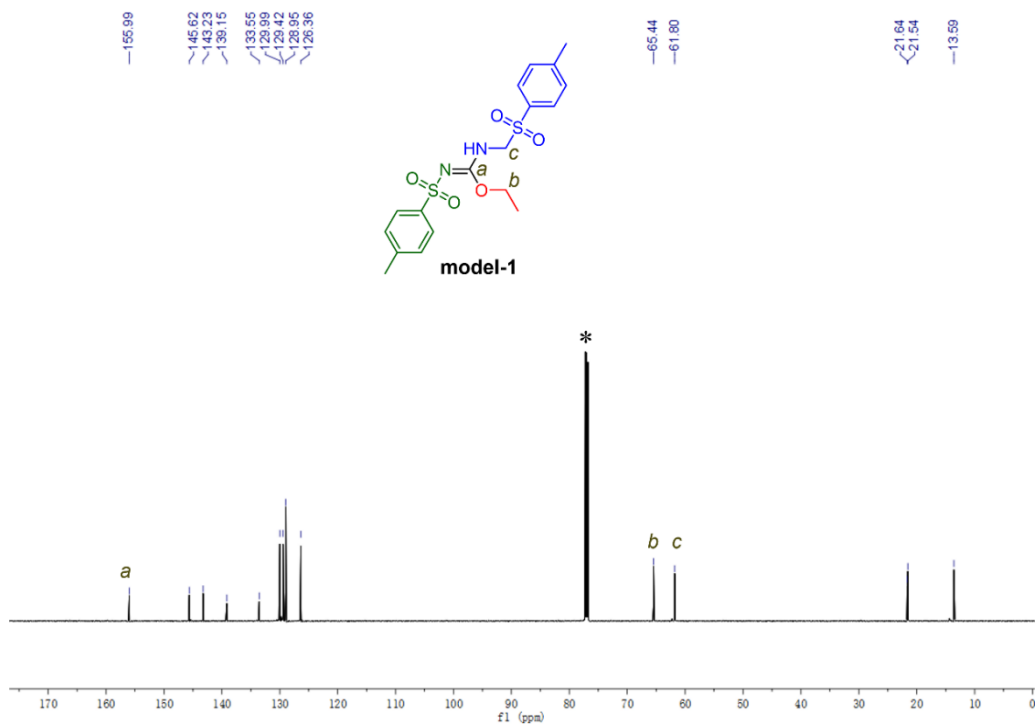


Figure S2. ^{13}C NMR spectrum of **model-1** in CDCl₃. The solvent peaks are marked with asterisks.

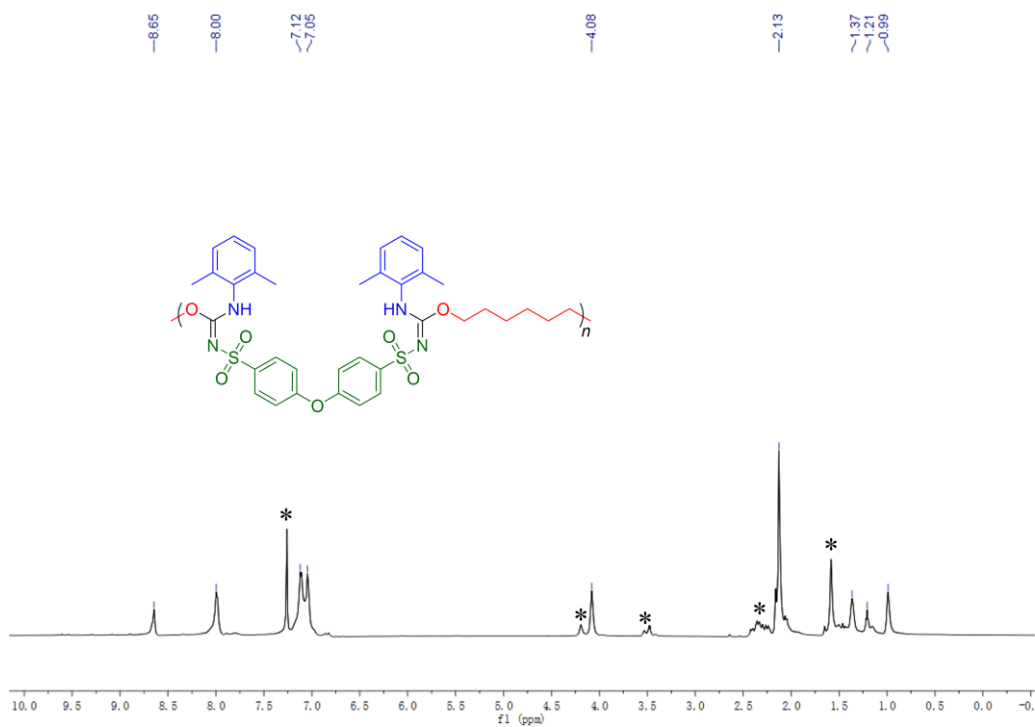


Figure S3. ¹H NMR spectrum of P1c2a3a in CDCl₃. The solvent peaks are marked with asterisks.

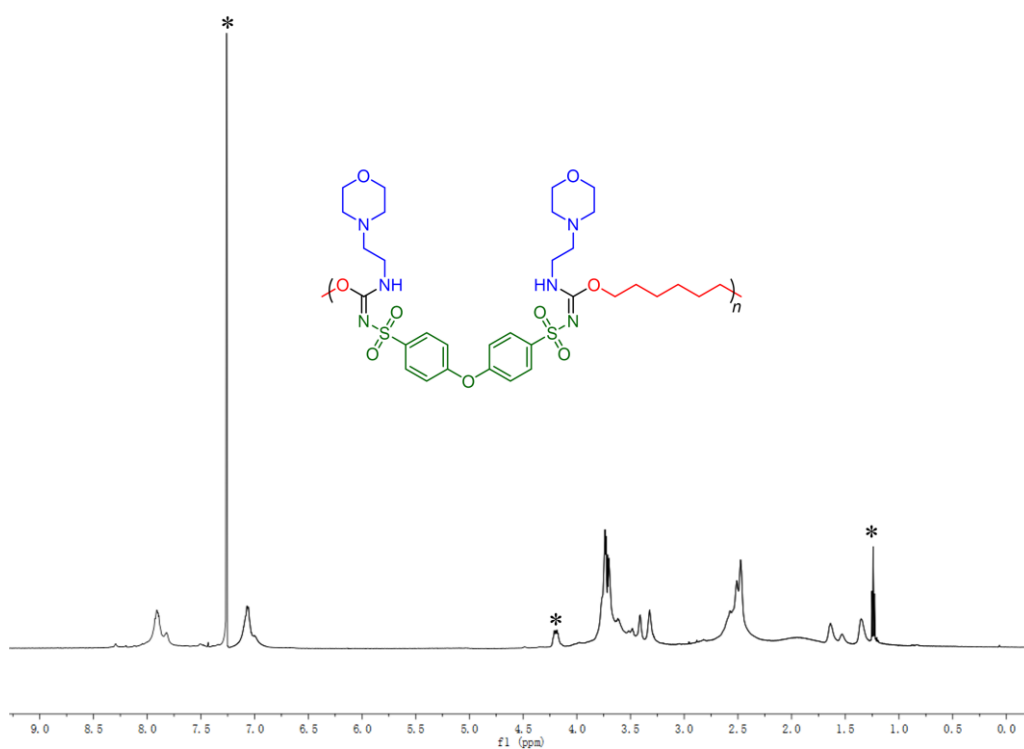


Figure S4. ¹H NMR spectrum of P1d2a3a in CDCl₃. The solvent peaks are marked with asterisks.

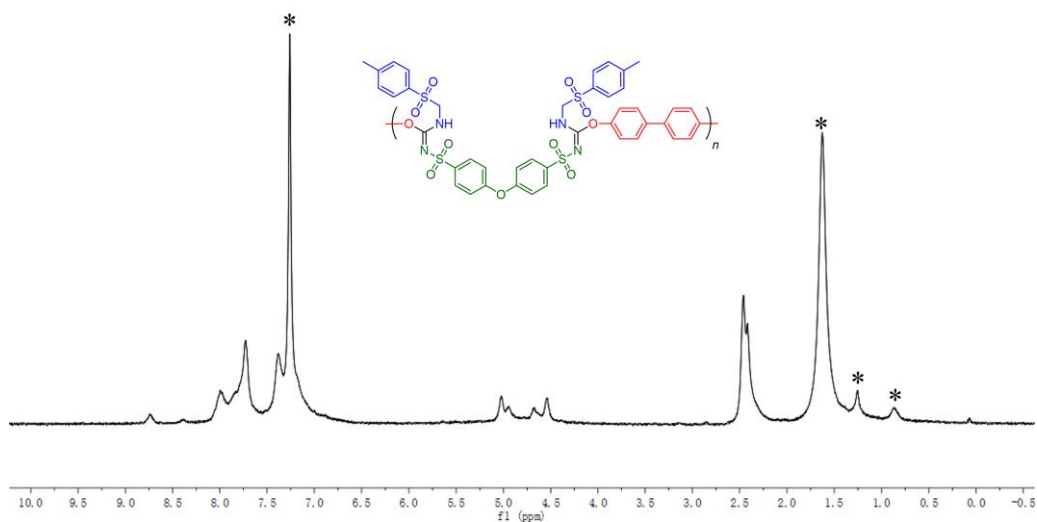


Figure S5. ^1H NMR spectrum of **P1a2a3b** in CDCl_3 . Isomeric units may exist in the polymer structure. The solvent peaks are marked with asterisks.

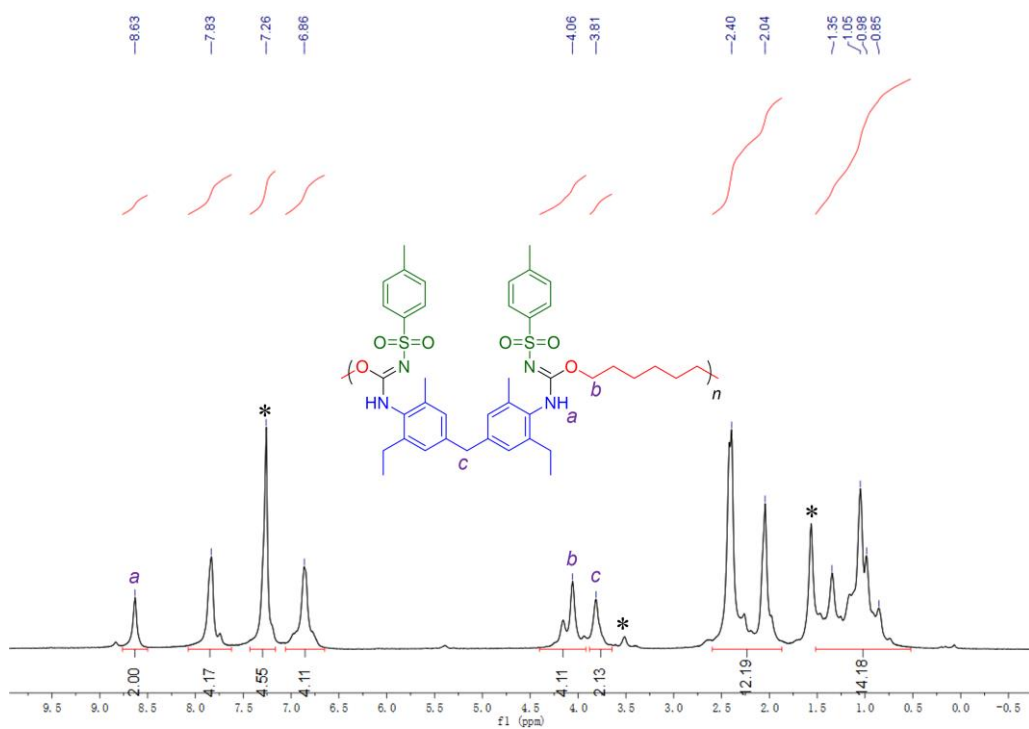


Figure S6. ^1H NMR spectrum of **P1e2d3a** in CDCl_3 . The solvent peaks are marked with asterisks.

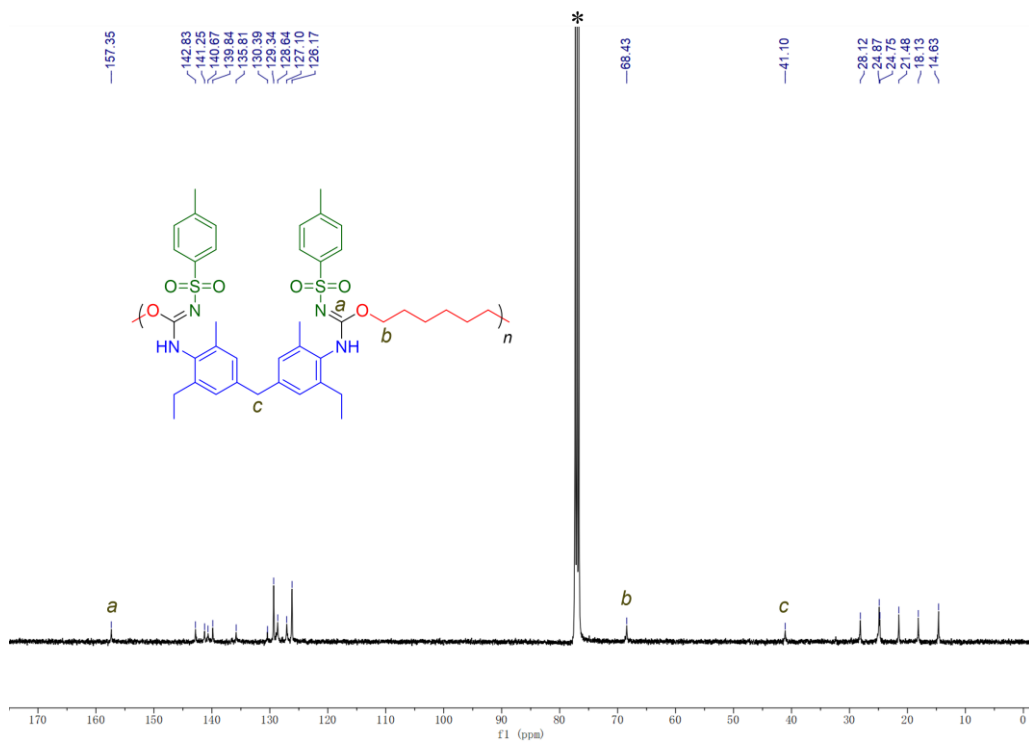


Figure S7. ^{13}C NMR spectrum of P1e2d3a in CDCl_3 . The solvent peaks are marked with asterisks.

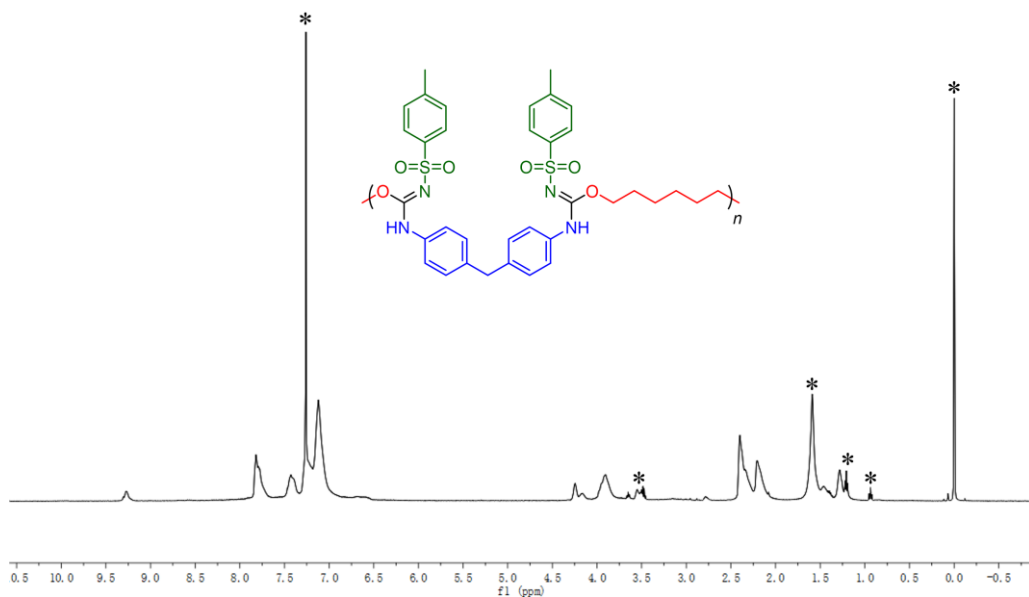


Figure S8. ^1H NMR spectrum of P1f2d3a in CDCl_3 . The solvent peaks are marked with asterisks.

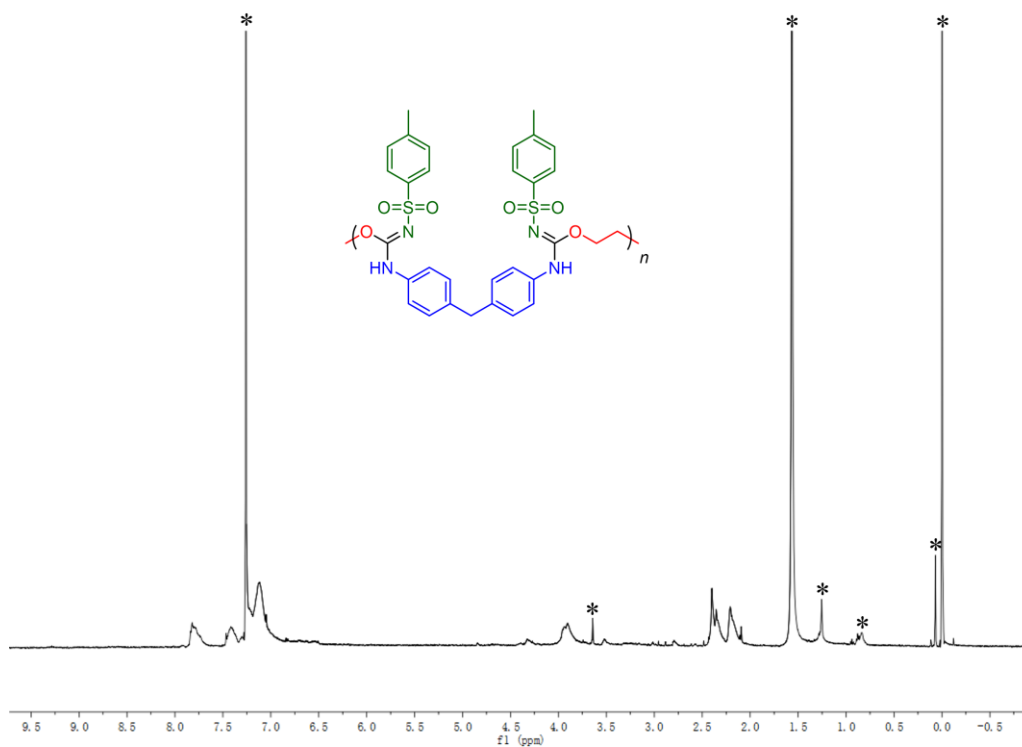


Figure S9. ¹H NMR spectrum of P1f2d3c in CDCl₃. The solvent peaks are marked with asterisks.

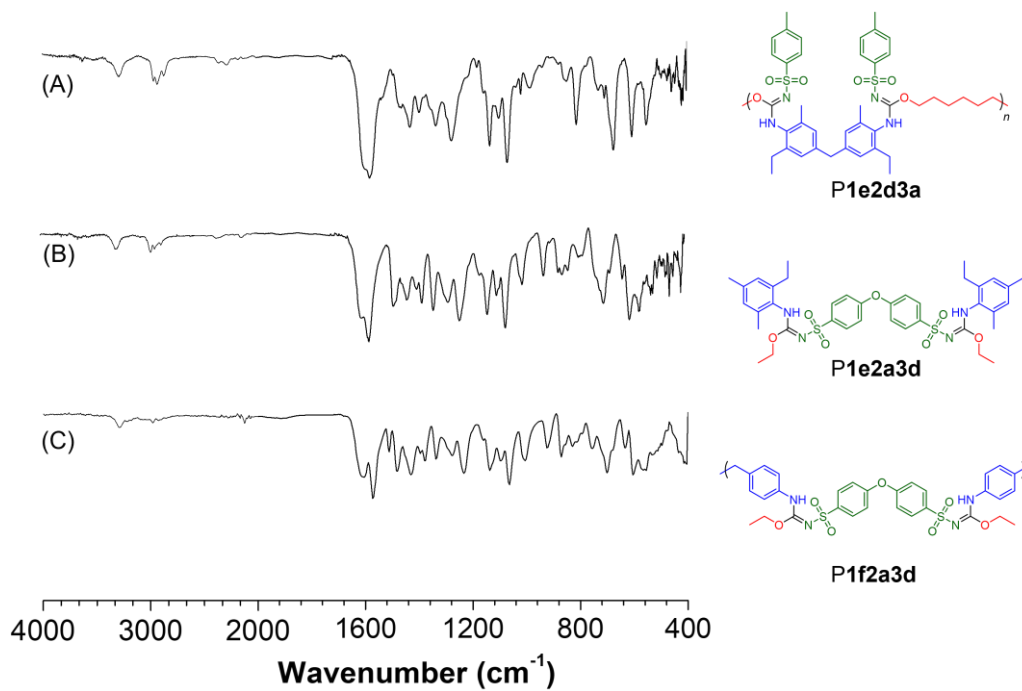


Figure S10. IR spectra of (A) P1e2d3a, (B) P1e2a3d, and (C) P1f2a3d.

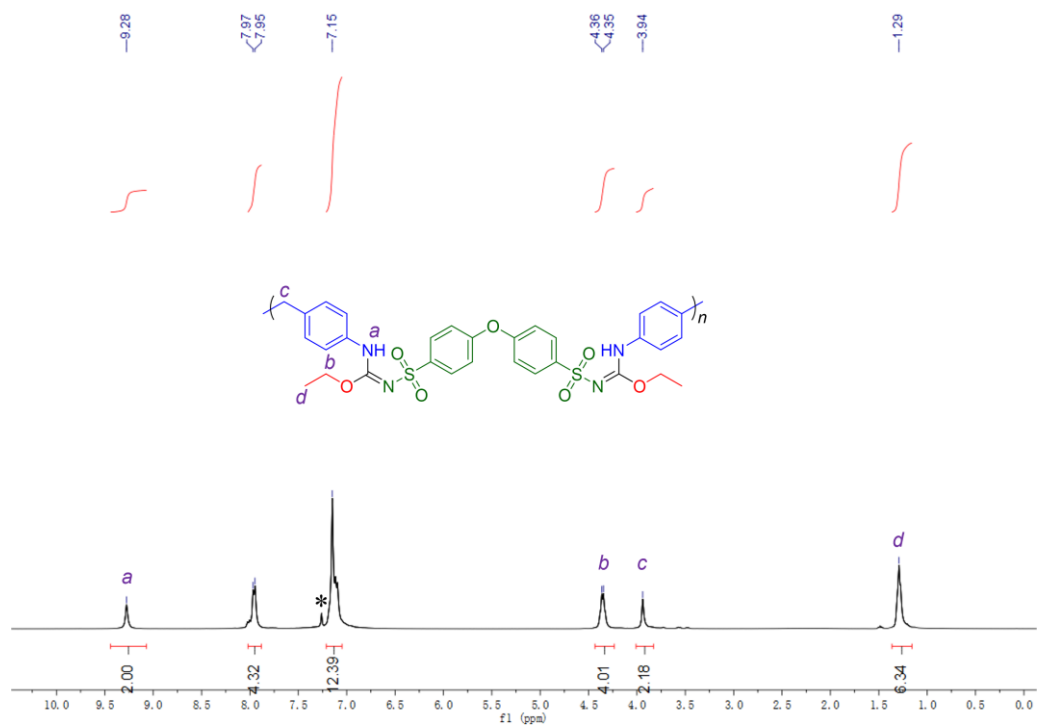


Figure S13. ^1H NMR spectrum of P1f2a3d in CDCl_3 . The solvent peaks are marked with asterisks.

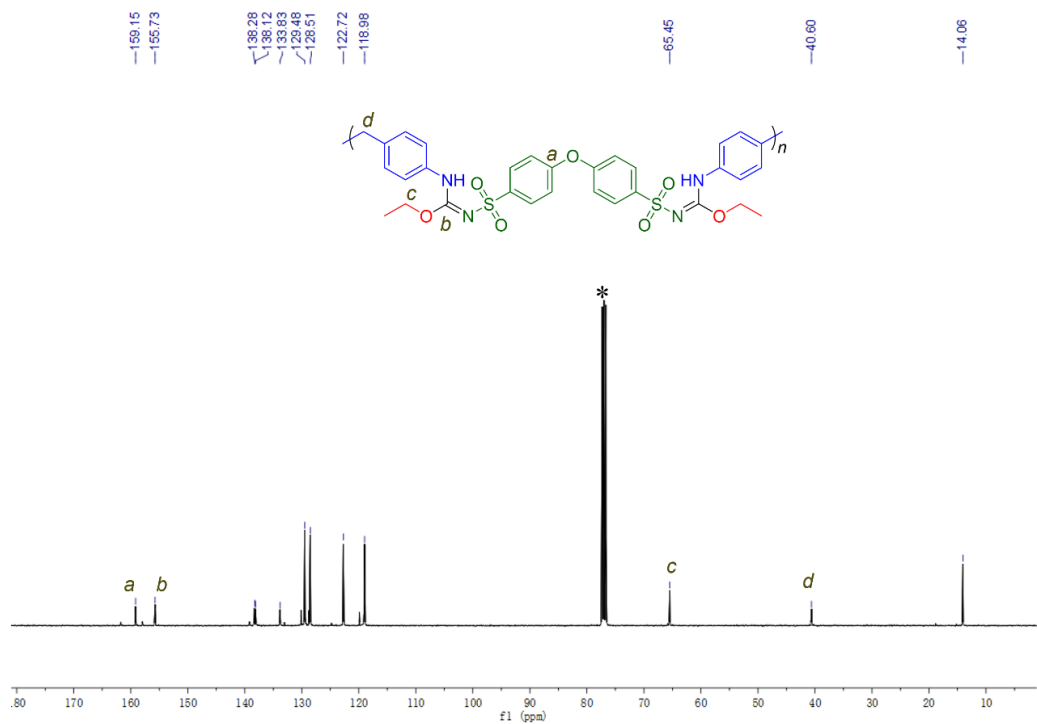


Figure S14. ^{13}C NMR spectrum of P1f2a3d in CDCl_3 . The solvent peaks are marked with asterisks.

References

- 1 Qin, A. J.; Liu, Y.; Tang, B. Z. Regioselective Metal-Free Click Polymerization of Azides and Alkynes. *Macromolecular Chemistry and Physics*, **2015**, *216*, 818-828.
- 2 Fu, W.; Kong, L.; Shi, J.; Tong, B.; Cai, Z.; Zhi, J.; Dong, Y. Synthesis of Poly(amine–furan–arylene)s through a One-Pot Catalyst-Free in Situ Cyclopolymerization of Diisocyanide, Dialkylacetylene Dicarboxylates, and Dialdehyde. *Macromolecules*, **2019**, *52*, 729-737.
- 3 Jiang, T.; Gu, Z.-Y.; Yin, L.; Wang, S.-Y.; Ji, S.-J. Cobalt(II)-Catalyzed Isocyanide Insertion Reaction with Sulfonyl Azides in Alcohols: Synthesis of Sulfonyl Isoureas. *The Journal of Organic Chemistry*, **2017**, *82*, 7913-7919.