

Facile Polymerization of Water and Triple-bond Based Monomers towards Functional Polyamides

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Materials. *N*-Bromosuccinimide was recrystallized before use. 4,4'-Methylenebis(2-ethyl-6-methylaniline) (**7a**), 1,4-phenylenedimethanamine (**7b**), 1,4-diethynylbenzene (**8a**), bisphenol A, 4-bromobenzophenone, and other chemicals and reagents were purchased from Sigma-Aldrich or Alfa and used as received without further purification. THF and toluene were distilled under nitrogen at normal pressure from sodium benzophenone ketyl immediately prior to use. Et₃N was distilled and dried over potassium hydroxide. DMSO and DMF were extra-dry grade.

Instruments. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer as thin films on KBr pellets. ¹H and ¹³C NMR spectra were measured on a Bruker AV 500 or Bruker AV 400 spectrometer in DMSO-*d*₆ using tetramethylsilane (TMS; $\delta = 0$) as internal reference. Relative weight-average and number-average molecular weights (M_w and M_n) and polydispersity indices ($\bar{D}$, M_w/M_n) of the polymers were estimated by a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with refractive index (RI) detector, using a set of monodisperse polymethyl methacrylate as calibration standards and DMF as the eluent at a flow rate of 1.0 mL/min. Thermal stabilities were evaluated by measuring thermogravimetric analysis (TGA) thermograms on a PerkinElmer TGA 7 under dry nitrogen at a heating rate of 10 °C/min. Refractive indices of the polymers were measured on J. A. Woollam V-VASE variable angle ellipsometry system with a region from 400 to 1700 nm. The polymer films were prepared by spin coating using THF as the solvent on crystalline silicon. UV-vis spectra were measured on a Varian VARY 100 Bio UV-vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

Monomer Preparation. In order to obtain a series of polyamides, A₂ (**1a** and **1b**) + B₂ (**2a**, **2b** and **2c**) + H₂O co-monomer strategies were used (A and B refer to the diisocyanides and

bis(bromoalkyne)s monomers respectively, Scheme 1). Monomers **1a**, **2a** and water were used as model monomers to optimize the polymerization conditions, and monomers **1b**, **2b**, and **2c** were applied to prove the universality and robustness of this polymerization. The synthetic routes to monomers **1** and **2** are shown in Schemes S1 and S2 and the detailed synthetic procedures are shown below.

Monomers **1** was prepared by slight modification of literature procedures.¹ The synthesis procedure of **1b** is resemble with that of **1a**. The detailed method for the synthesis of **1a** was given here as an example.

1,1-Bis(3-ethyl-4-isocyano-5-methylphenyl)methane (**1a**). A 50% aqueous solution of sodium hydroxide (15 mL) was added to the vigorously stirred DCM solution (15 mL) containing 4,4'-methylenebis(2-ethyl-6-methylaniline) (14.100 g, 50 mmol), chloroform (4.022 mL, 50 mmol), and TEBA chloride (227.8 mg, 1 mmol). The mixture was heated at 40 °C for 12 hours. The reaction was monitored by thin-layer chromatography (TLC). Afterwards, the reaction mixture was cooled down to room temperature, and cold water (100 mL) was added. The aqueous phase was extracted with methylene chloride. The organic layer was washed with concentrated sodium bicarbonate solution and dried over magnesium sulphate. The drying agent was filtered off, and the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography to give **1a**.

Characterization data of 1a: White powder of **1a** was obtained in 31.7% yield (4.790 g). FT-IR (KBr), ν (cm⁻¹): 2115 (C $\equiv$ N stretching). ¹H NMR (500 MHz, DMSO-*d*₆) δ (TMS, ppm): 7.11 (d, *J* = 10 Hz, 2H), 3.90 (s, 1H), 2.67 (q, *J* = 10.0 Hz, 2H), 2.32 (s, 3H), 1.17 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (125 MHz, DMSO) δ (ppm): 168.46 (s), 142.43 (s), 140.60 (s), 135.19 (s), 128.81 (s), 127.32 (s), 25.59 (s), 18.88 (s), 14.30 (s).

Characterization data of 1b: Yellow powder of **1b** was obtained in 28.9% yield (2.251 g). FT-IR (KBr), ν (cm^{-1}): 2160 ($\text{C}\equiv\text{N}$ stretching). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (TMS, ppm): 7.43 (s, 2H), 4.91-4.85 (m, 2H). ^{13}C NMR (125 MHz, DMSO) δ (ppm): 157.16 (s), 133.79 (s), 127.84 (s), 44.97 (s).

Monomer **2** was prepared by slight modification of literature procedures.² The synthetic procedures of **2b-2c** are resemble with that of **2a**. The detailed method for the synthesis of **2a** was given here as an example.

1,4-Bis(bromoethynyl)benzene (**2a**). 1,4-Diethynylbenzene (1.790 g, 14.2 mmol) was dissolved in acetone (60 mL), and *N*-bromosuccinimide (7.590 g, 42.6 mmol) and AgNO_3 (531 mg, 3.1 mmol) was added. The reaction mixture was stirred overnight at room temperature in dark. Afterwards, the solution was concentrated under reduced pressure and the crude product was purified by a silica gel column chromatography using petroleum ether (PE) as eluent. Light yellow powder of **2a** was obtained.

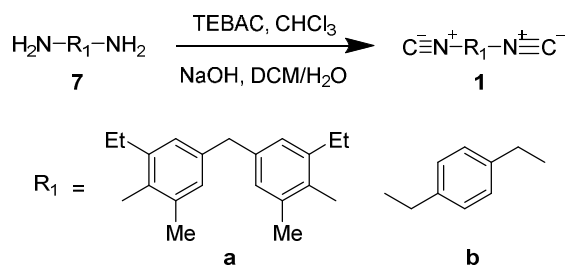
Characterization data of 2a: White powder of **2a** was obtained in 85.0% yield (4.828 g). IR (KBr), ν (cm^{-1}): 2194 ($\text{C}\equiv\text{C}$ stretching). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (TMS, ppm): 7.49 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ (ppm): 132.52 (s), 122.83 (s), 79.62 (s), 55.92 (s), 31.15 (s).

Characterization data of 2b: Yellow solid of **2b** was obtained in 61.3% yield (5.664 g). IR (KBr), ν (cm^{-1}): 2223 ($\text{C}\equiv\text{C}$ stretching). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (TMS, ppm): 7.13 (d, $J = 10.0$ Hz, 4H), 6.87 (d, $J = 5.0$ Hz, 4H), 4.80 (s, 4H), 1.59 (s, 6H). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ (ppm): 155.42 (s), 143.80 (s), 127.95 (s), 114.59 (s), 76.38 (s), 56.60 (s), 41.72 (s), 31.12 (s).

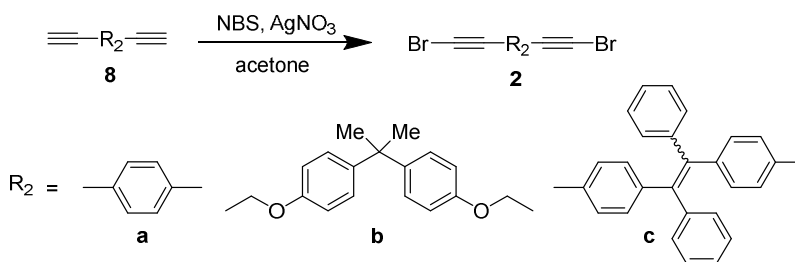
Characterization data of 2c: White powder of **2c** was obtained in 65.0% yield (6.994 g). IR (KBr), ν (cm^{-1}): 2205 ($\text{C}\equiv\text{C}$ stretching). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.26-7.23 (m, 4H),

7.18-7.15 (m, 6H), 7.05 – 6.94 (m, 8H). ^{13}C NMR (125 MHz, DMSO) δ 144.11 (s), 142.85 (s), 141.05 (s), 133.74 (s), 132.33 (s), 131.10 (s), 128.44 (s), 127.40 (s), 127.11 (s), 120.59 (s), 80.05 (s), 53.73 (s).

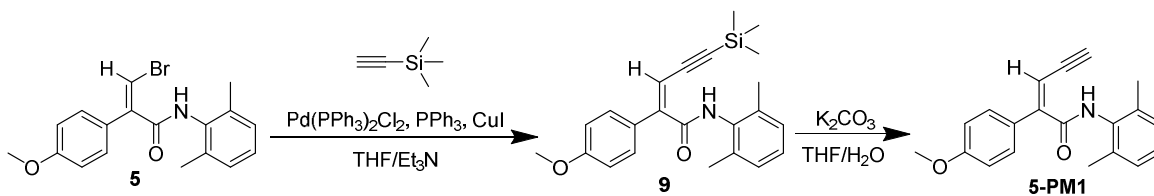
Scheme S1. Synthetic route to diisocyanides **1.**



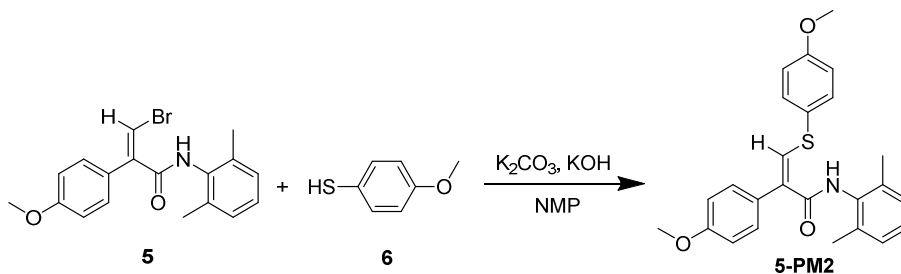
Scheme S2. Synthetic route to dibromoalkynes **2.**



Scheme S3. Synthetic route to model compound **5-PM1.**



Scheme S4. Synthetic route to model compound **5-PM2.**



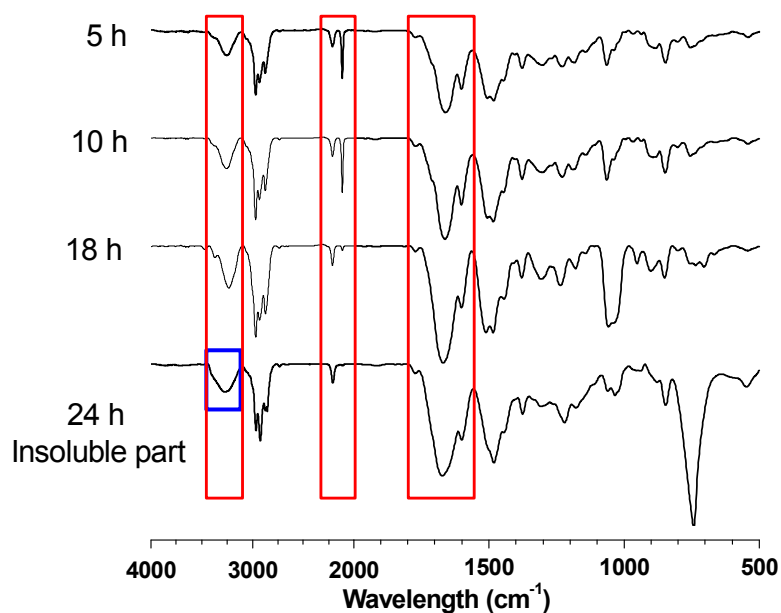


Figure S1. FT-IR spectra of polymers obtained at 100 °C at different reaction time.

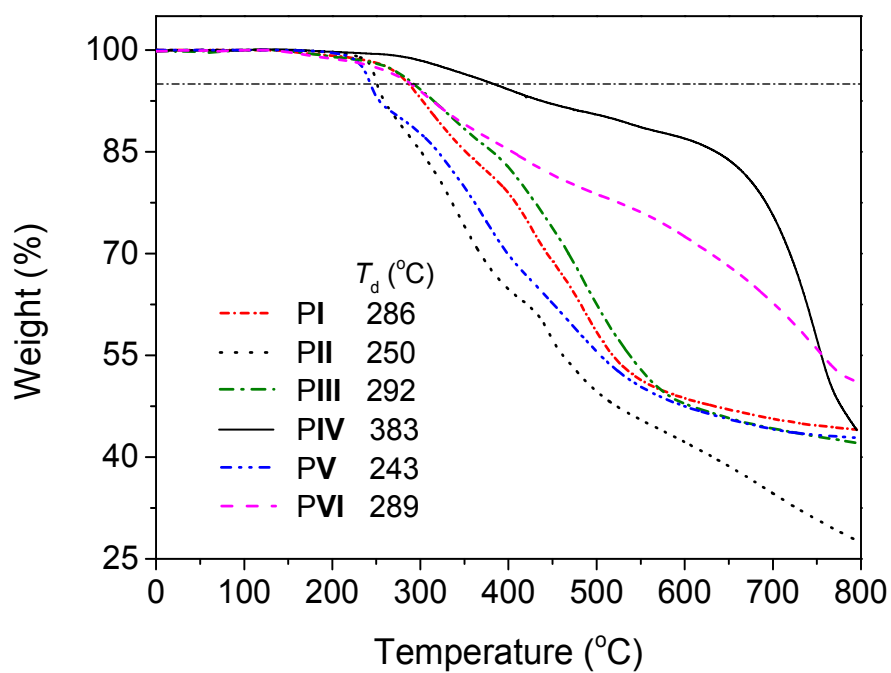


Figure S2. TGA thermograms of polymers PI-PVI. T_d represents the temperature of 5% weights loss.

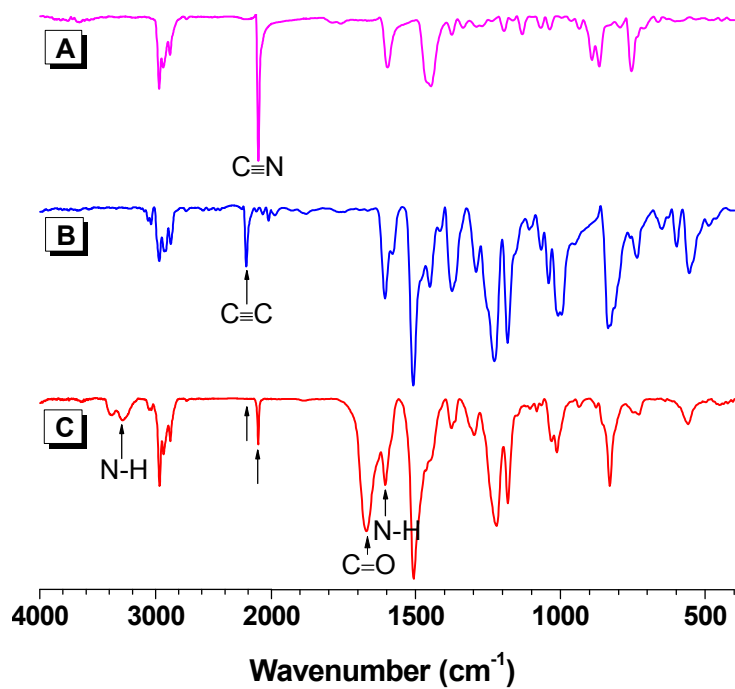


Figure S3. FT-IR spectra of **1a** (A), **2b** (B) and **PII** (C).

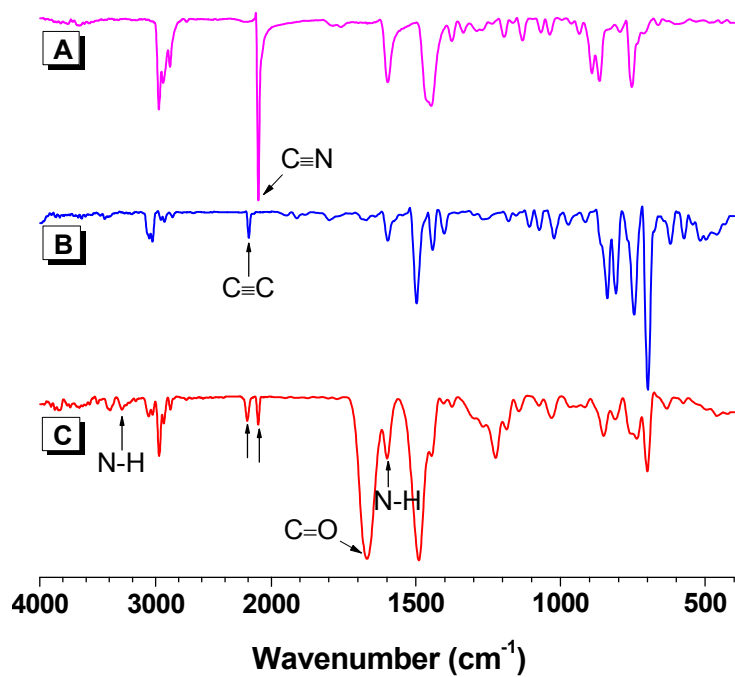


Figure S4. FT-IR spectra of **1a** (A), **2c** (B) and **PIII** (C).

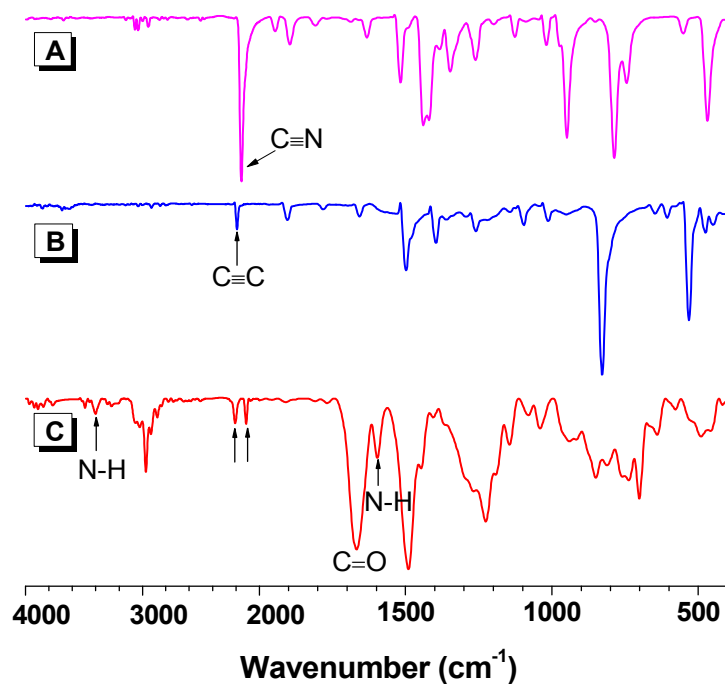


Figure S5. FT-IR spectra of **1b** (A), **2a** (B) and PIV (C).

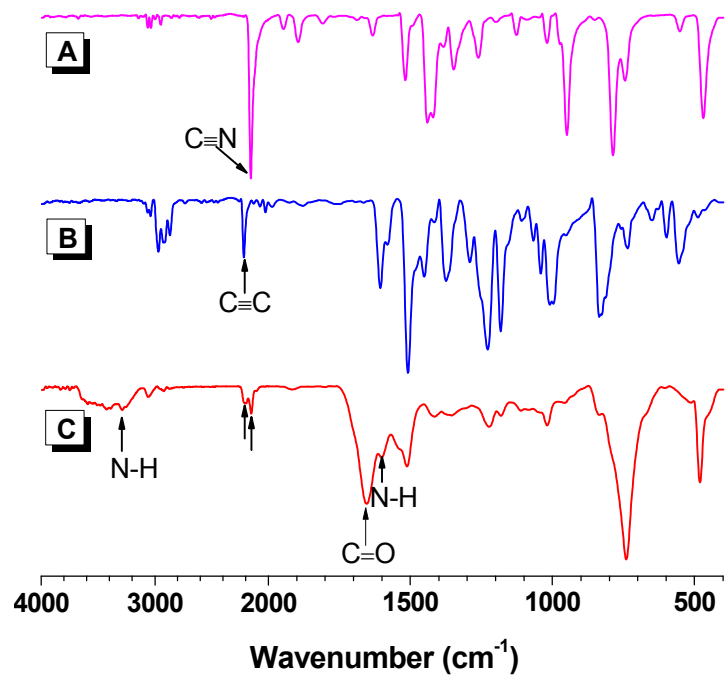


Figure S6. FT-IR spectra of **1b** (A), **2b** (B) and PV (C).

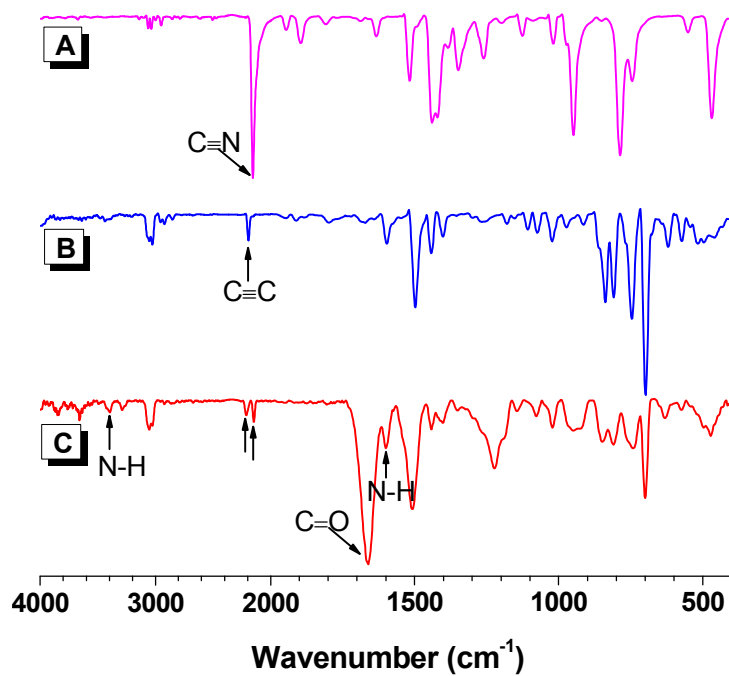


Figure S7. FT-IR spectra of **1b** (A), **2c** (B) and **PVI** (C).

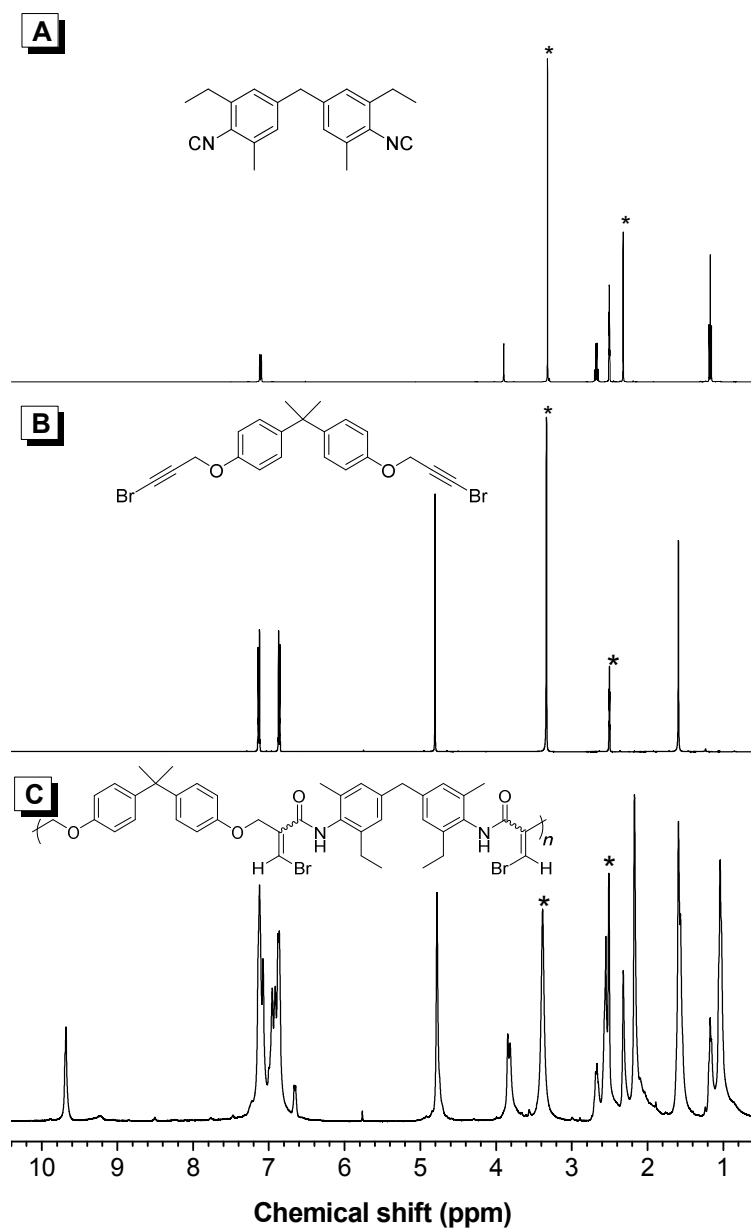


Figure S8. ^1H NMR spectra of **1a** (A), **2b** (B) and **PII** (C) in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

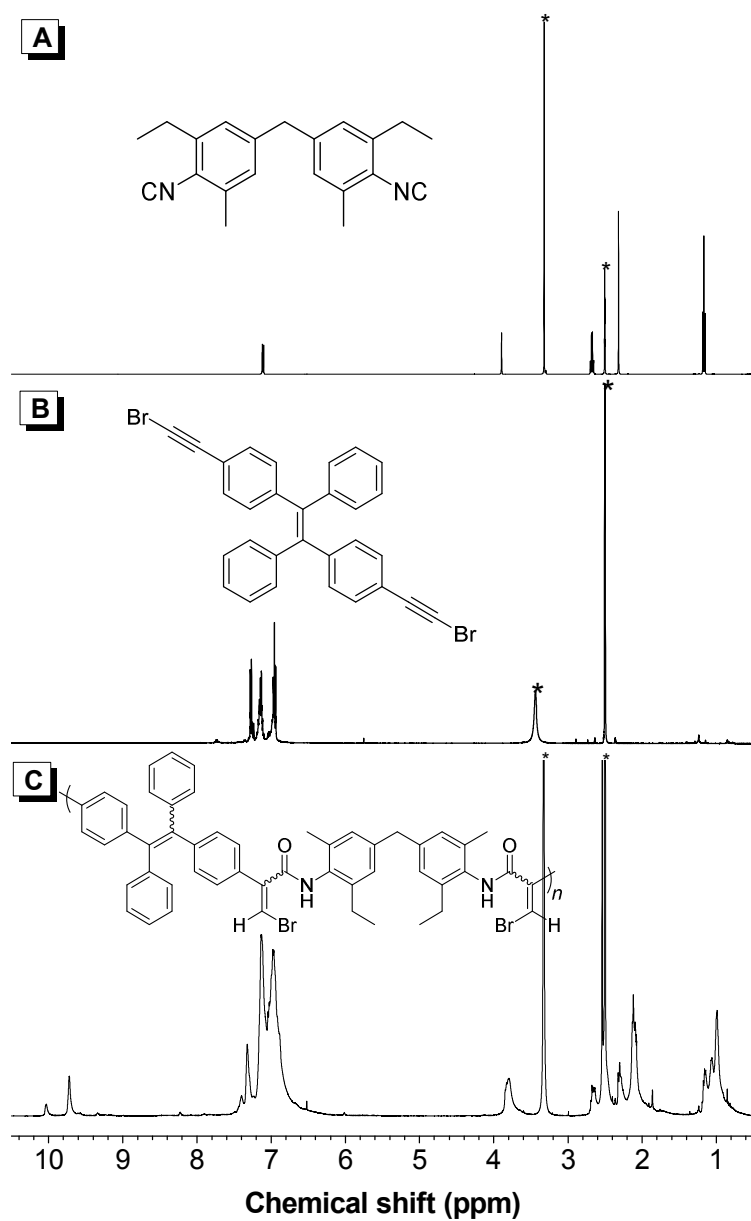


Figure S9. ^1H NMR spectra of **1a** (A), **2c** (B) and **PIH** (C) in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

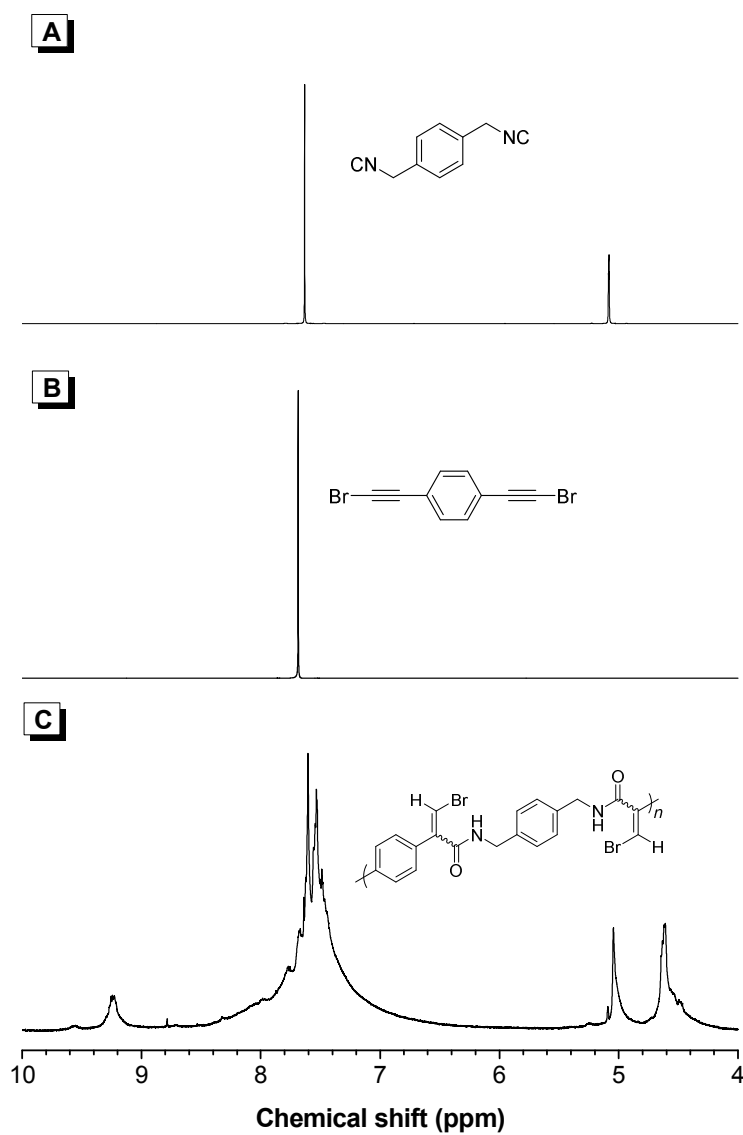


Figure S10. ^1H NMR spectra of **1b** (A), **2a** (B) and **PIV** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

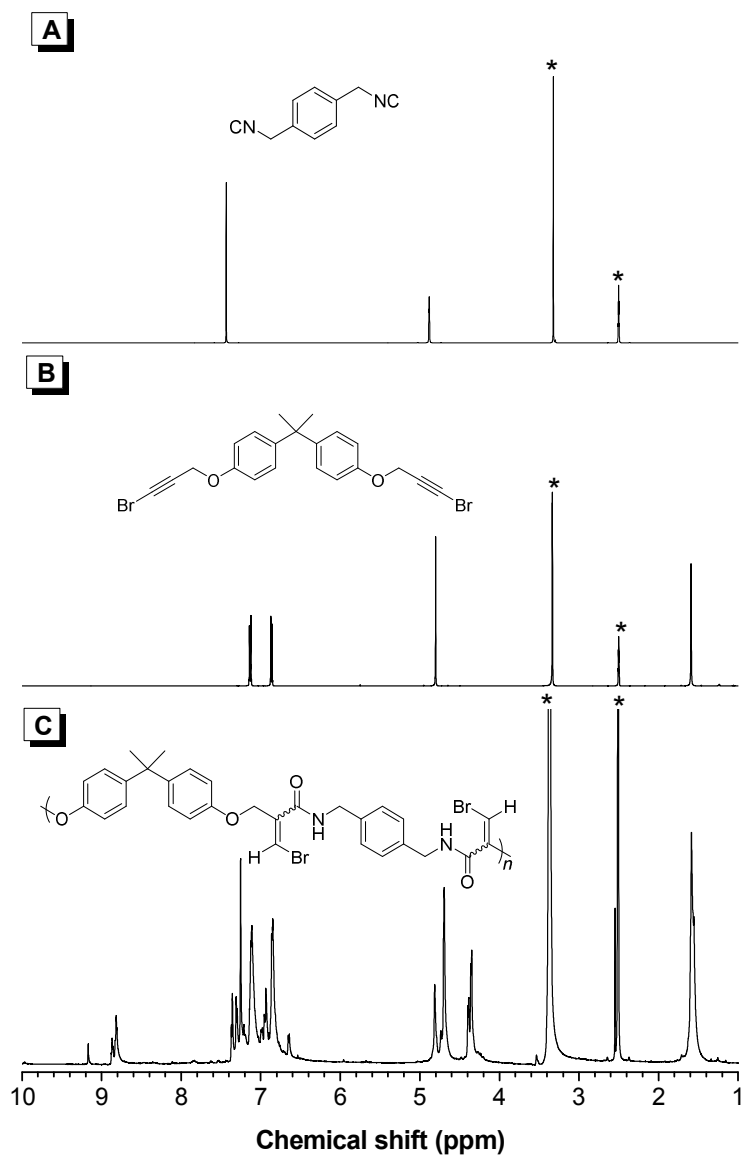


Figure S11. ^1H NMR spectra of **1b** (A), **2b** (B) and PV (C) in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

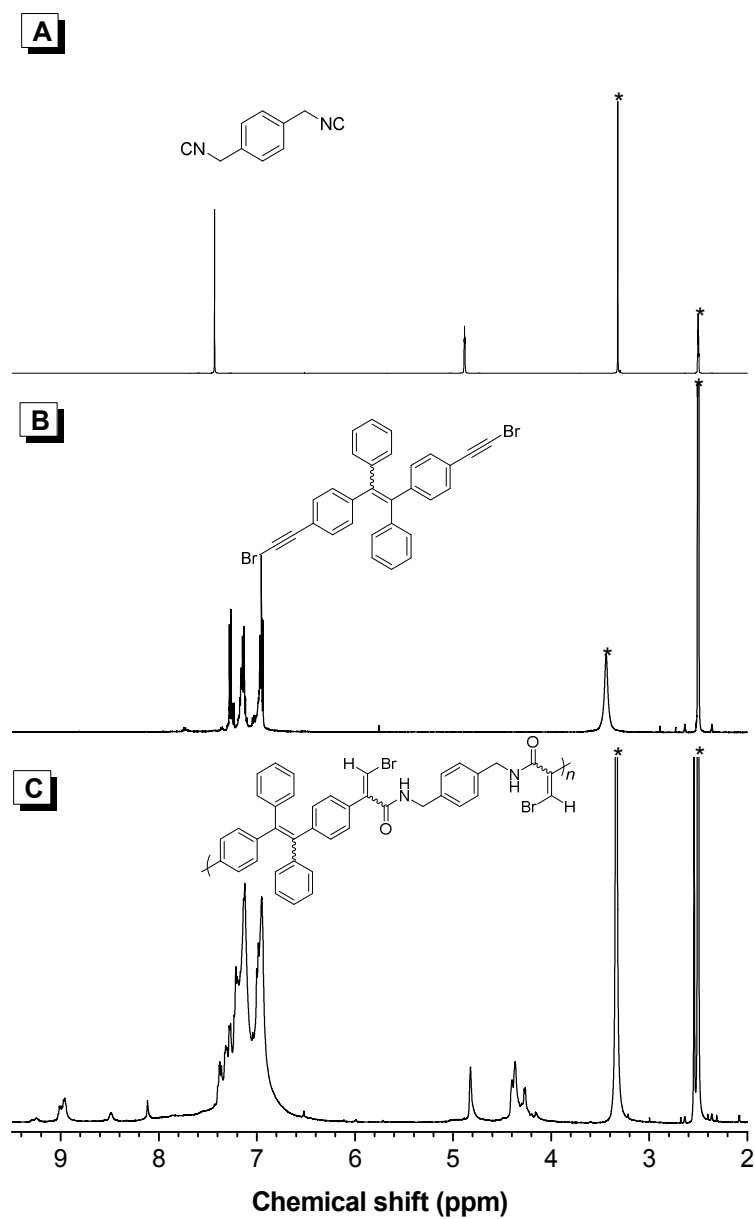


Figure S12. ^1H NMR spectra of **1b** (A), **2c** (B) and **PVI** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

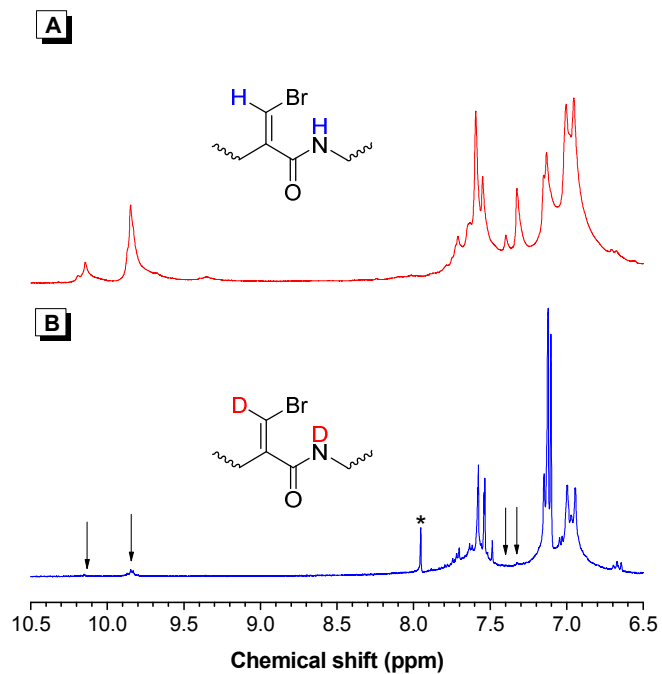


Figure S13. ^1H NMR spectra of polymers prepared using H_2O (A) and D_2O (B) as co-monomer in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

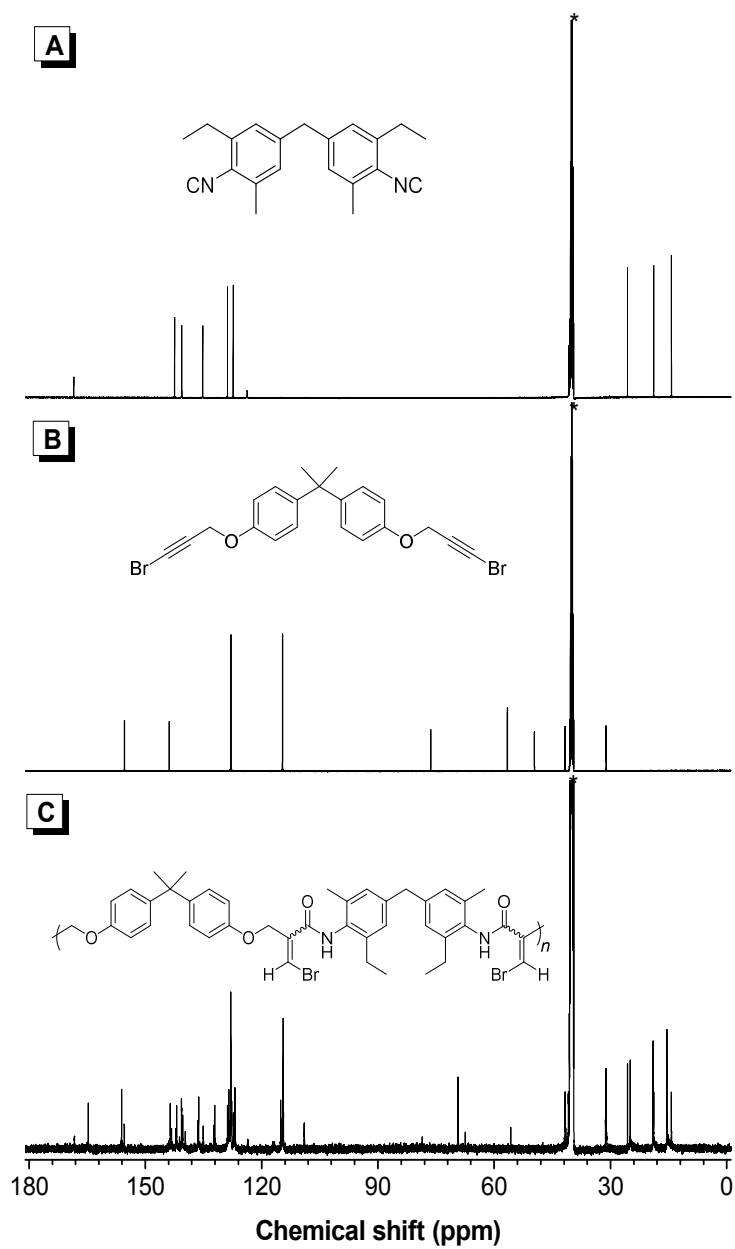


Figure S14. ^{13}C NMR spectra of **1a** (A), **2b** (B) and **PII** (C) in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

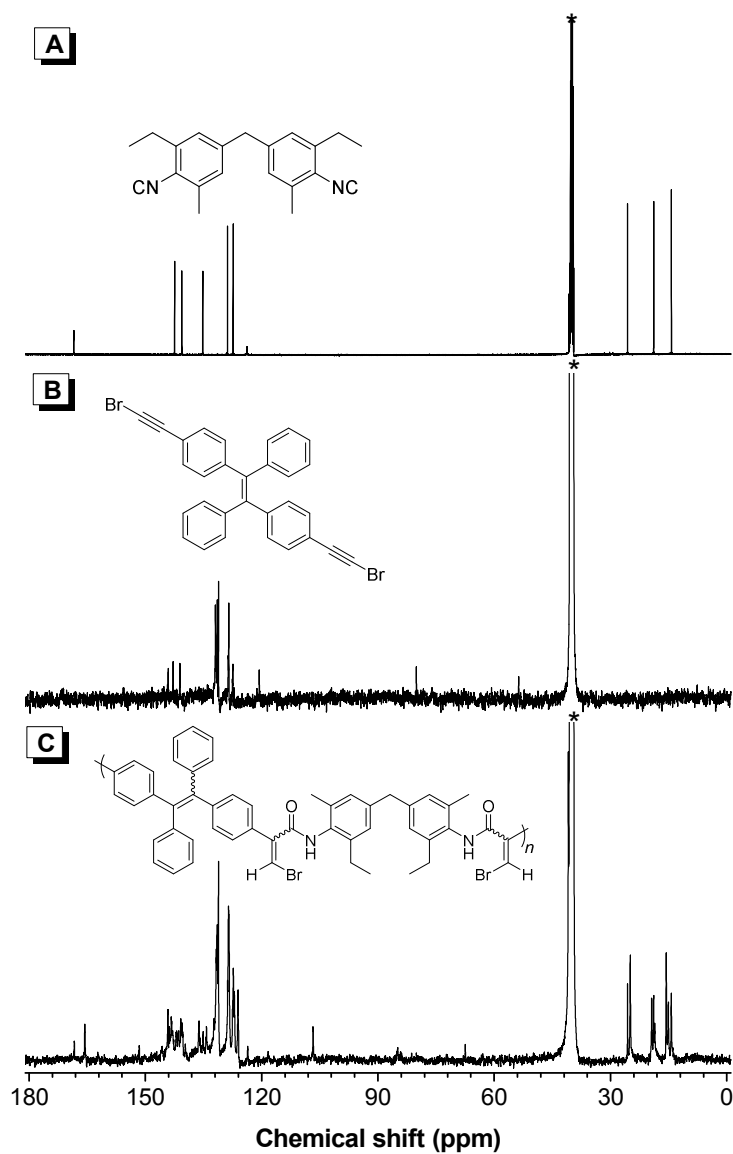


Figure S15. ^{13}C NMR spectra of **1a** (A), **2c** (B) and **PIII** (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

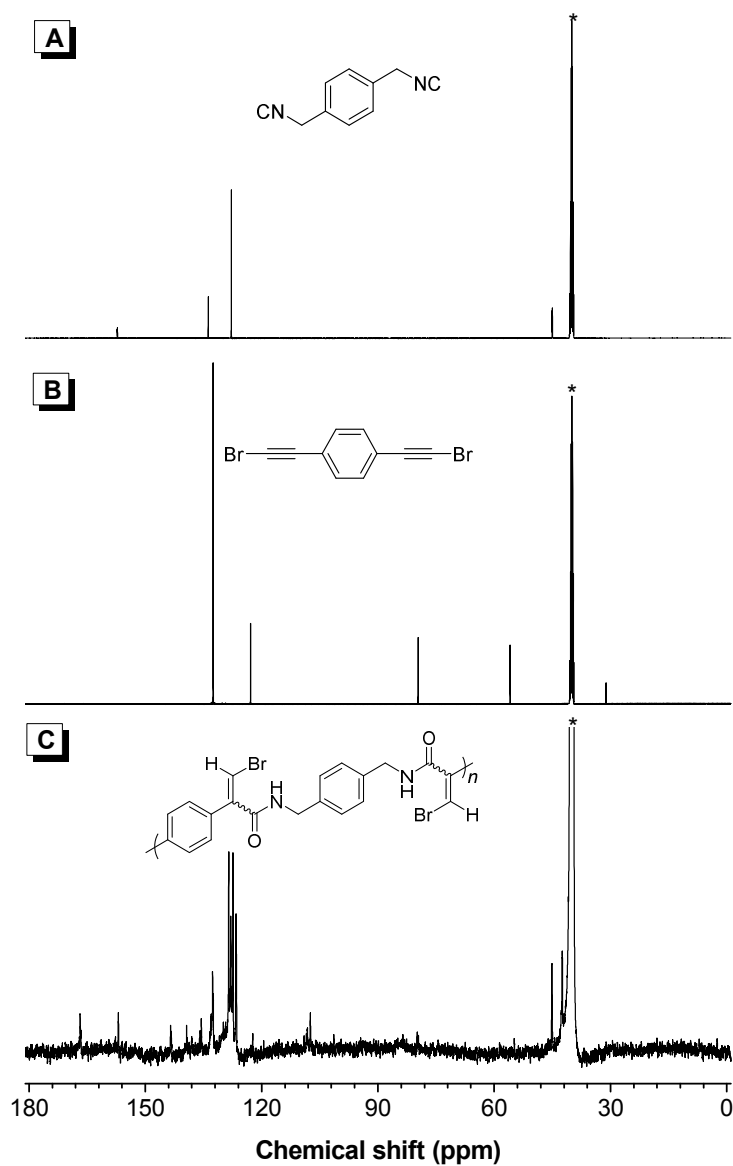


Figure S16. ^{13}C NMR spectra of **1b** (A), **2a** (B) and PIV (C) in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

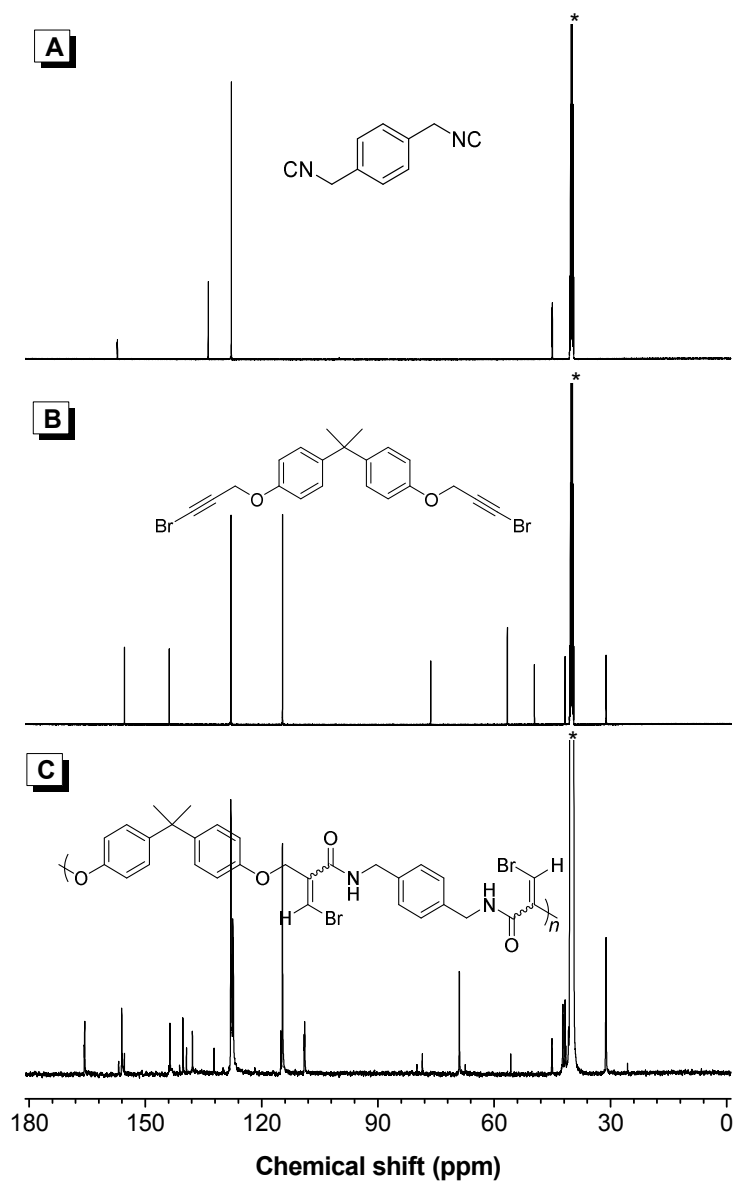


Figure S17. ^{13}C NMR spectra of **1b** (A), **2b** (B) and PV (C) in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

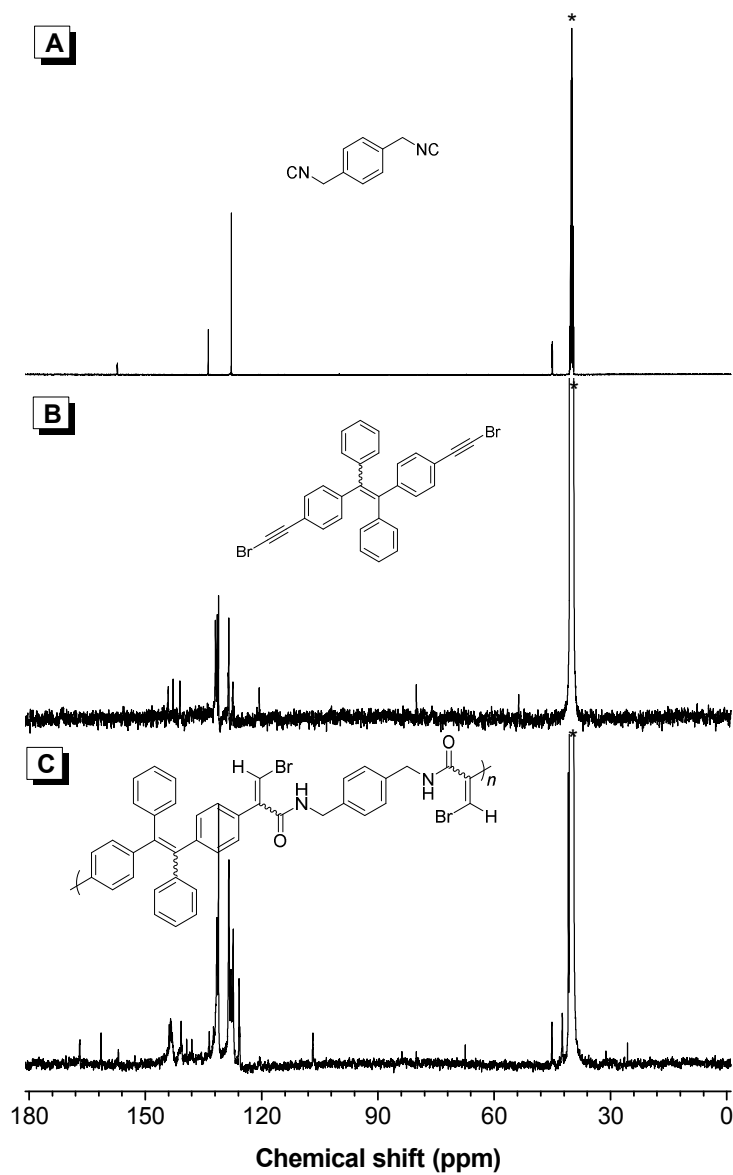


Figure S18. ^{13}C NMR spectra of **1b** (A), **2c** (B) and **PVI** (C) in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

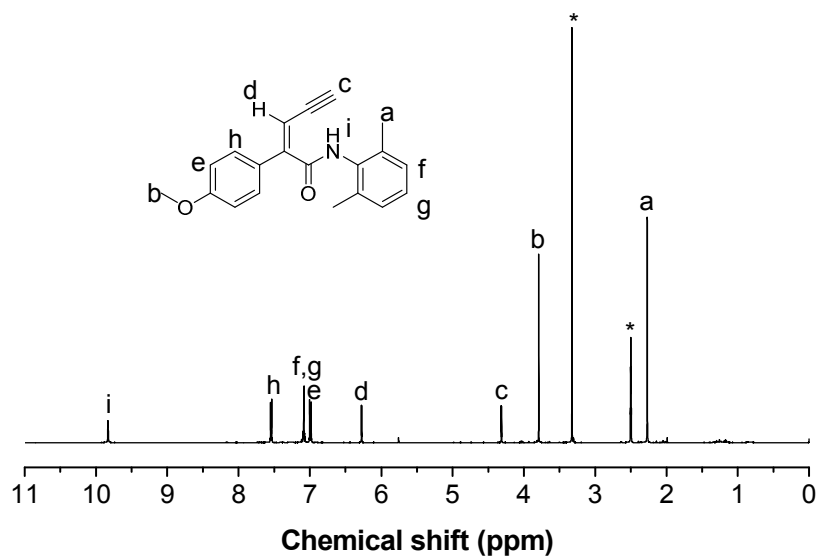


Figure S19. ^1H NMR spectrum of **7** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

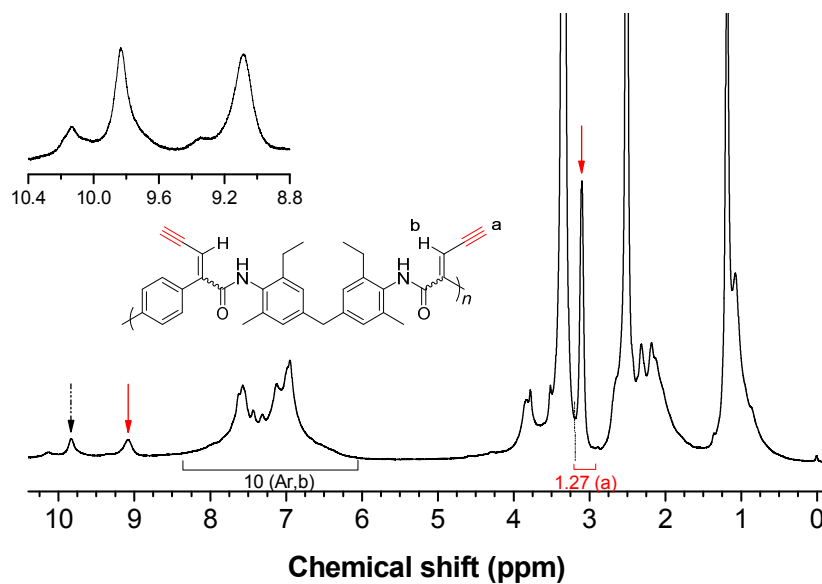


Figure S20. ^1H NMR spectrum of **PI-PM1** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

The grafting degree of **PI-PM2** is arranged as x , then un-reacted part accounts for $(1 - x)$,

$$\frac{2x}{10x + 10(1 - x)} = \frac{1.27}{10}$$

$$x = 0.635$$

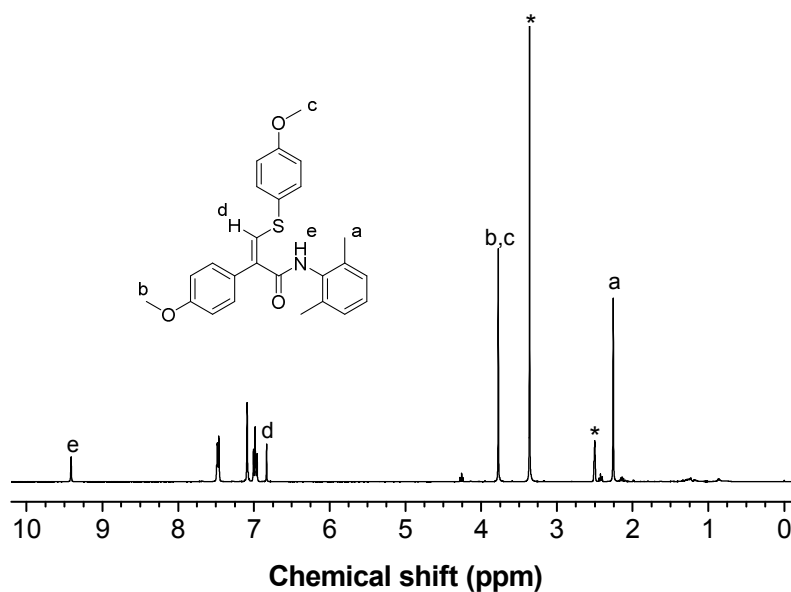


Figure S21. ^1H NMR spectrum of **9** in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

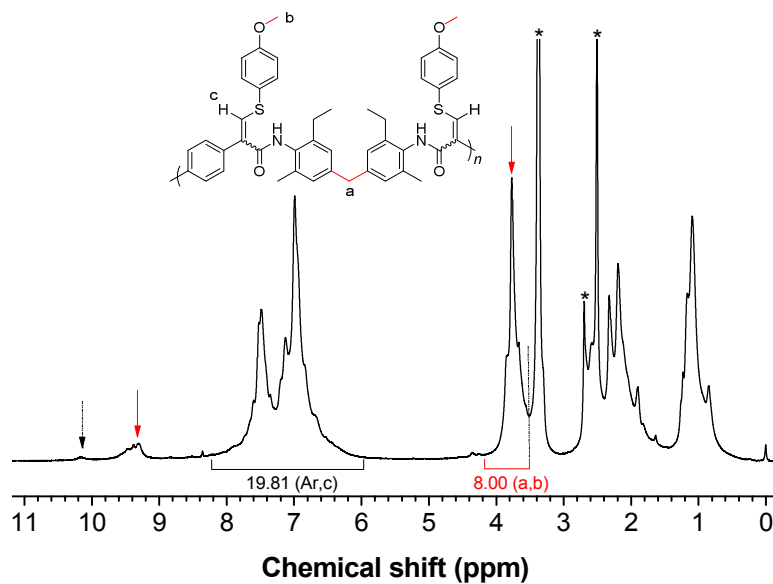


Figure S22. ^1H NMR spectrum of **PI-PM2** in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

The grafting degree of PI-PM2 is arranged as x , then un-reacted part accounts for $(1 - x)$,

$$\frac{8x + 2(1 - x)}{18x + 10(1 - x)} = \frac{8}{19.81}$$

$$x = 0.736$$

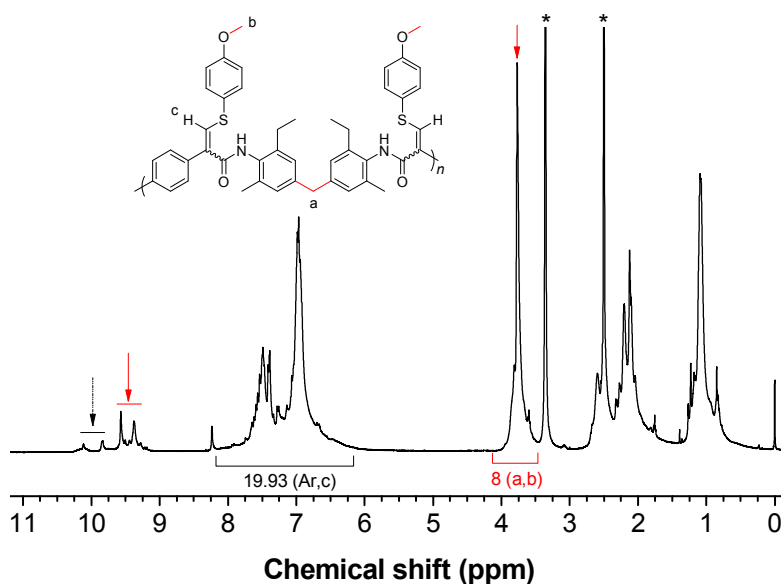


Figure S23. ^1H NMR spectrum of PI-PM3 in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

The grafting degree of PI-PM2 is arranged as x , then un-reacted part accounts for $(1 - x)$,

$$\frac{8x + 2(1 - x)}{18x + 10(1 - x)} = \frac{8}{19.93}$$

$$x = 0.727$$

Table S1. Effect of the amount of water on the polymerization of diisocyanide **1a** and dibromoalkyne **2a**.^a

entry	$V_{\text{H}_2\text{O}}$ (μL)	yield (%)	M_w ^b	$\bar{D}$ ^b
1	7.2	40.4	16400	2.23
2	100	51.2	17900	2.18
3	200	44.4	18800	2.25

^a Carried out in DMSO at 90 °C for 10 h under nitrogen ($[\mathbf{1a}]/[\mathbf{2a}] = 1.5$, $[\text{CsF}]/[\mathbf{2a}] = 2$, $[\mathbf{2a}] = 0.1 \text{ M}$). ^b M_w and $\bar{D}$ (M_w/M_n) of polymers were estimated by GPC in DMF containing 0.05 M LiBr on the basis of a polymethyl methacrylate calibration.

References

- (1) Zakrzewski, J.; Krawczyk, M. Synthesis and Pesticidal Properties of Thio and Seleno Analogs of Some Common Urea Herbicides. *Phosphorus, Sulfur Silicon Relat. Elem.*, **2009**, *184*, 1880-1903.
- (2) Zatolochnaya, O. V.; Gevorgyan, V. Synthesis of Fluoro- and Perfluoroalkyl Arenes via Palladium-Catalyzed [4+2] Benzannulation Reaction. *Org. Lett.*, **2013**, *15*, 2562-2565.