

Transition metal-free thiol-yne click polymerization toward *Z*-stereoregular poly(vinylene sulfide)s

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Contents

Table S1. Effect of base amount on the polymerization of 1a and 2a	S3
Table S2. Effect of monomer concentration on the polymerization of 1a and 2a	S3
Fig. S1 FT-IR spectra of monomers (A) 1a and (B) 2b and their polymer (C) P1a2b	S4
Fig. S2 FT-IR spectra of monomers (A) 1a and (B) 2c and their polymer (C) P1a2c	S4
Fig. S3 FT-IR spectra of monomers (A) 1b and (B) 2b and their polymer (C) P1b2b	S5
Fig. S4 ¹ H NMR spectra of monomer (A) 1a and (B) 2b and their polymer (C) P1a2b in CDCl ₃ . The solvent peaks are marked with asterisks.	S5
Fig. S5 ¹ H NMR spectra of monomer (A) 1a and (B) 2c and their polymer (C) P1a2c in CDCl ₃ . The solvent peaks are marked with asterisks.	S6
Fig. S6 ¹ H NMR spectra of monomer (A) 1b and (B) 2b and their polymer (C) P1b2b in CDCl ₃ . The solvent peaks are marked with asterisks.	S6
Fig. S7 ¹³ C NMR spectra of monomer (A) 1a and (B) 2b and their polymer (C) P1a2b in CDCl ₃ . The solvent peaks are marked with asterisks.	S7
Fig. S8 ¹³ C NMR spectra of monomer (A) 1a and (B) 2c and their polymer (C) P1a2c in CDCl ₃ . The solvent peaks are marked with asterisks.	S7
Fig. S9 ¹³ C NMR spectra of monomer (A) 1b and (B) 2b and their polymer (C) P1b2b in CDCl ₃ . The solvent peaks are marked with asterisks.	S8
Fig. S10 ¹ H NMR spectra of P1a2b in CDCl ₃ : (A) freshly prepared, (B) stored under ambient conditions for one year. The solvent peaks are marked with asterisks.	S8
Fig. S11 ¹ H NMR spectra of P1b2b in CDCl ₃ : (A) freshly prepared, (B) stored under ambient conditions for one year. The solvent peaks are marked with asterisks.	S9
Fig. S12 PL spectra of P1b2b in THF and THF/water mixtures with different water fractions (<i>f_w</i>). Polymer concentration: 10 ⁻⁵ M. Excitation wavelength: 352 nm.	S9

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

Entry	K ₃ PO ₄ (equiv)	Yield (%)	<i>M</i> _w ^b	<i>D</i> ^b
1	1	92	9600	1.80
2	2	95	10 600	1.66
3 ^c	3	95	18 500	1.61

^aCarried out in NMP in the presence of K₃PO₄ under nitrogen at 100 °C for 24 h, [**1a**] = [**2a**] = 0.1 M. ^bEstimated by GPC in THF on the basis of a linear polystyrene calibration, polydispersity index (*D*) = *M*_w/*M*_n. ^cData taken from Table 2, entry 5.

Table S2. Effect of monomer concentration on the polymerization of **1a** and **2a**^a

Entry	[1a] (M)	Yield (%)	<i>M</i> _w ^b	<i>D</i> ^b
1	0.025	60	5500	1.45
2	0.05	92	8000	1.66
3 ^c	0.1	95	18 500	1.61
4	0.2	91	15 000	1.87

^aCarried out in NMP in the presence of K₃PO₄ under nitrogen at 100 °C for 24 h, [**1a**] = [**2a**], [K₃PO₄] = 3[**1a**]. ^bEstimated by GPC in THF on the basis of a linear polystyrene calibration, polydispersity index (*D*) = *M*_w/*M*_n. ^cData taken from Table 2, entry 5.

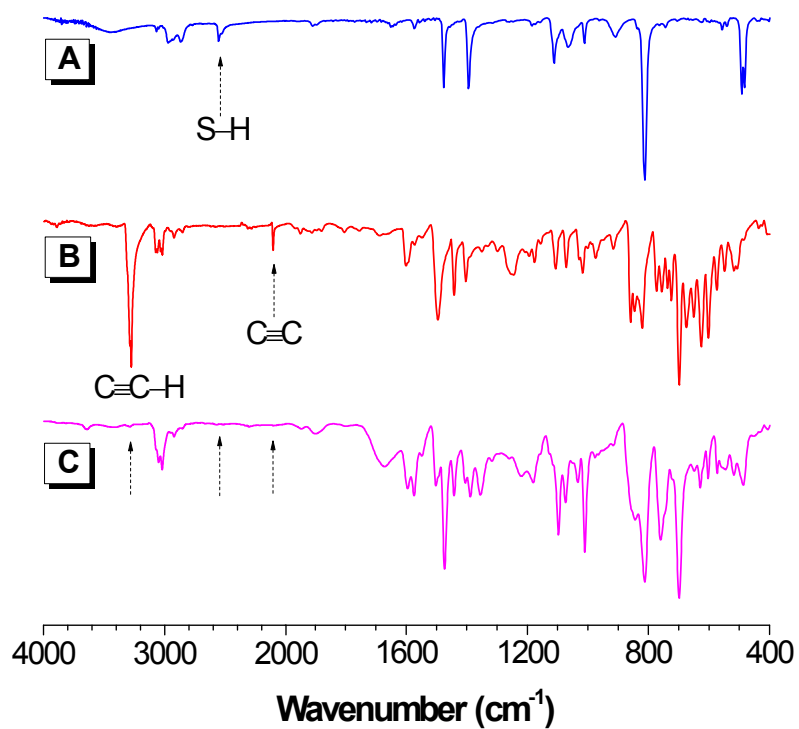


Fig. S1 FT-IR spectra of monomers (A) **1a** and (B) **2b** and their polymer (C) **P1a2b**

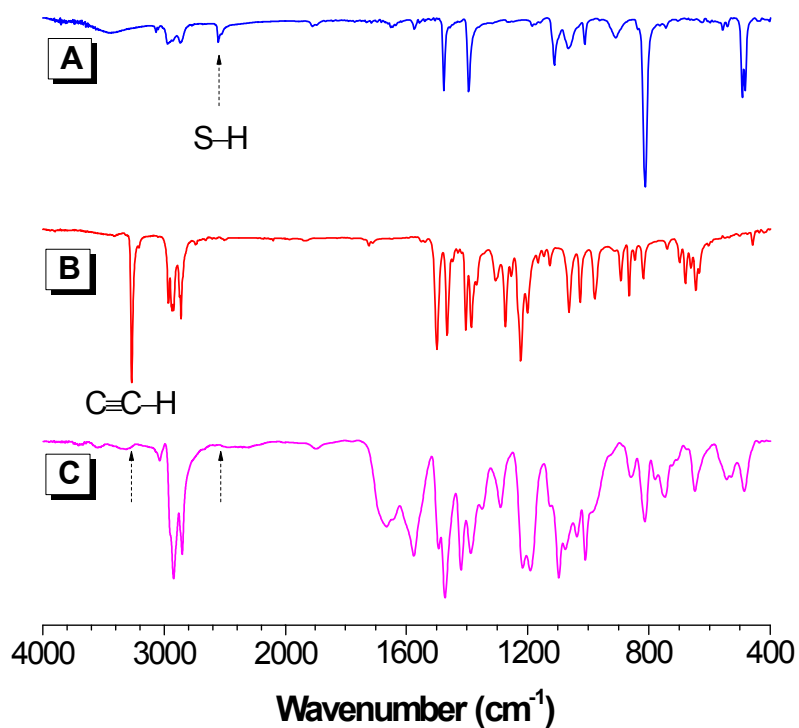


Fig. S2 FT-IR spectra of monomers (A) **1a** and (B) **2c** and their polymer (C) **P1a2c**

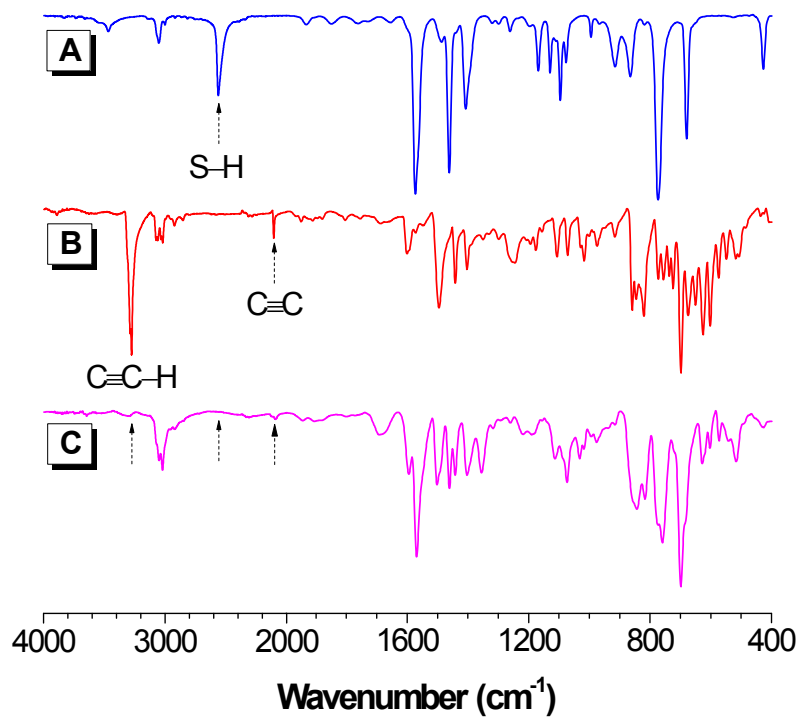


Fig. S3 FT-IR spectra of monomers (A) **1b** and (B) **2b** and their polymer (C) **P1b2b**

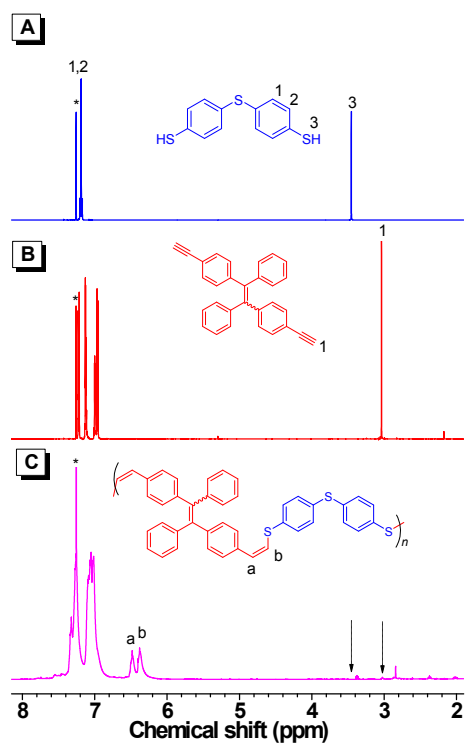


Fig. S4 ^1H NMR spectra of monomer (A) **1a** and (B) **2b** and their polymer (C) **P1a2b** in CDCl_3 . The solvent peaks are marked with asterisks.

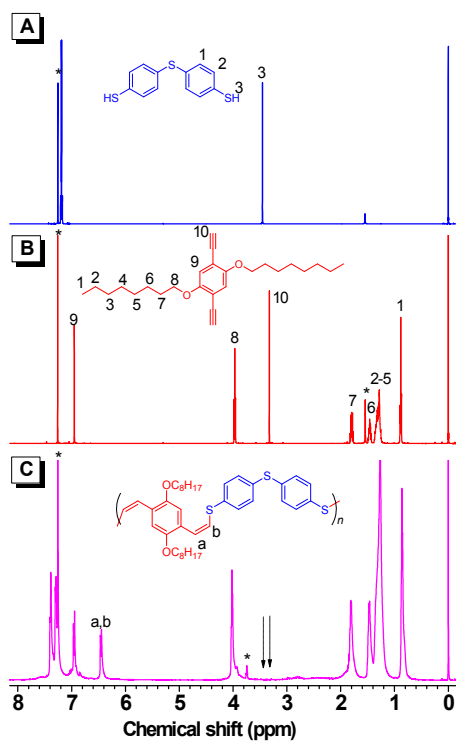


Fig. S5 ^1H NMR spectra of monomer (A) **1a** and (B) **2c** and their polymer (C) **P1a2c** in CDCl_3 . The solvent peaks are marked with asterisks.

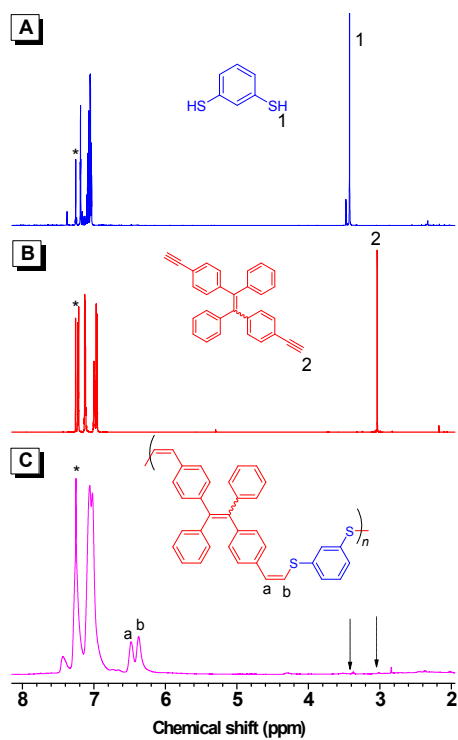


Fig. S6 ^1H NMR spectra of monomer (A) **1b** and (B) **2b** and their polymer (C) **P1b2b** in CDCl_3 . The solvent peaks are marked with asterisks.

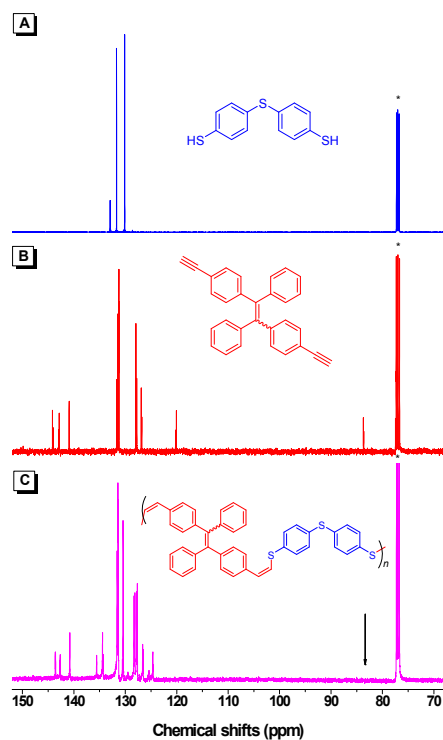


Fig. S7 ^{13}C NMR spectra of monomer (A) **1a** and (B) **2b** and their polymer (C) **P1a2b** in CDCl_3 . The solvent peaks are marked with asterisks.

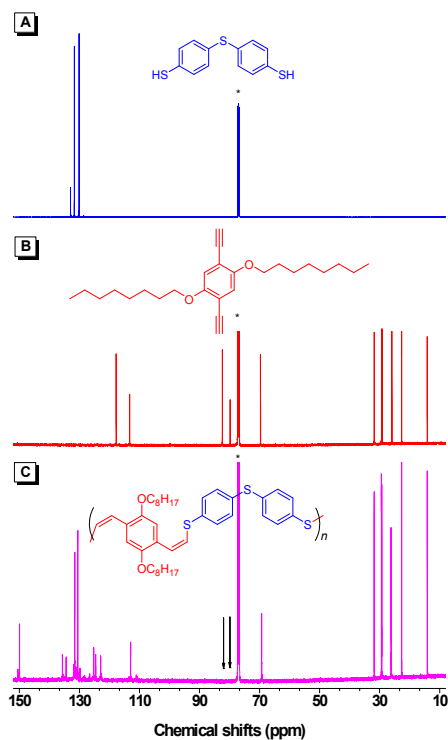


Fig. S8 ^{13}C NMR spectra of monomer (A) **1a** and (B) **2c** and their polymer (C) **P1a2c** in CDCl_3 . The solvent peaks are marked with asterisks.

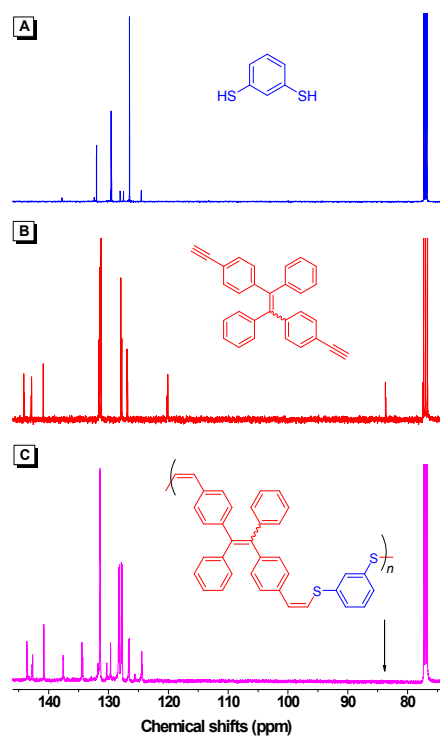


Fig. S9 ^{13}C NMR spectra of monomer (A) **1b** and (B) **2b** and their polymer (C) **P1b2b** in CDCl_3 . The solvent peaks are marked with asterisks.

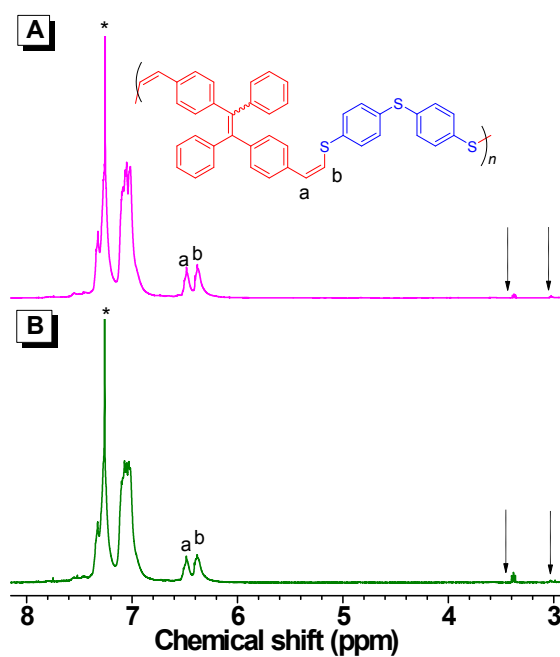


Fig. S10 ^1H NMR spectra of **P1a2b** in CDCl_3 : (A) freshly prepared, (B) stored under ambient conditions for one year. The solvent peaks are marked with asterisks.

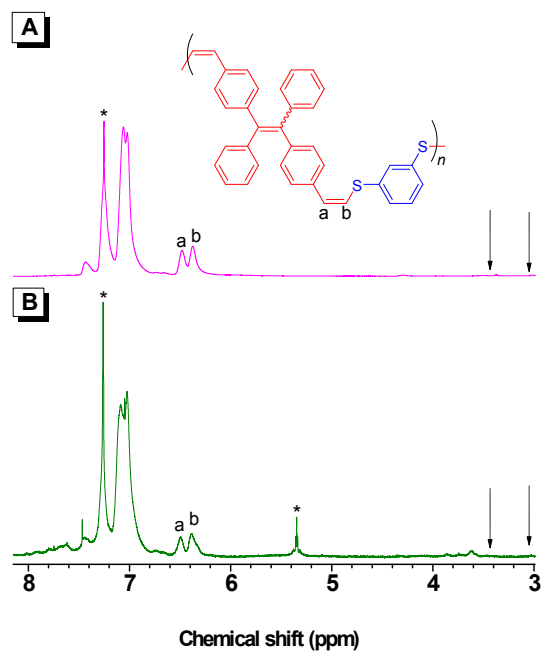


Fig. S11 ^1H NMR spectra of P1b2b in CDCl_3 : (A) freshly prepared, (B) stored under ambient conditions for one year. The solvent peaks are marked with asterisks.

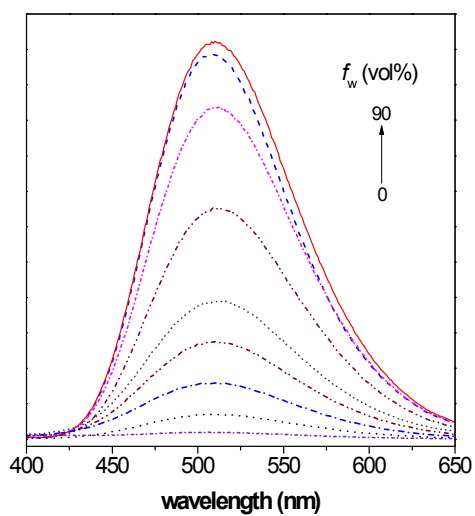


Fig. S12 PL spectra of P1b2b in THF and THF/water mixtures with different water fractions (f_w). Polymer concentration: 10^{-5} M. Excitation wavelength: 352 nm.