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

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

<table>
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<tr>
<th>Entry</th>
<th>K₃PO₄ (equiv)</th>
<th>Yield (%)</th>
<th>Mₘ</th>
<th>D</th>
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<td>1</td>
<td>92</td>
<td>9600</td>
<td>1.80</td>
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<tr>
<td>2</td>
<td>2</td>
<td>95</td>
<td>10 600</td>
<td>1.66</td>
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<td>3c</td>
<td>3</td>
<td>95</td>
<td>18 500</td>
<td>1.61</td>
</tr>
</tbody>
</table>

*a*Carried out in NMP in the presence of K₃PO₄ under nitrogen at 100 °C for 24 h, [1a] = [2a] = 0.1 M. *b*Estimated by GPC in THF on the basis of a linear polystyrene calibration, polydispersity index (D) = Mₘ/Mₙ. *c*Data taken from Table 2, entry 5.

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

<table>
<thead>
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<th>Entry</th>
<th>[1a] (M)</th>
<th>Yield (%)</th>
<th>Mₘ</th>
<th>D</th>
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<td>91</td>
<td>15 000</td>
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</table>

*a*Carried out in NMP in the presence of K₃PO₄ under nitrogen at 100 °C for 24 h, [1a] = [2a], [K₃PO₄] = 3[1a]. *b*Estimated by GPC in THF on the basis of a linear polystyrene calibration, polydispersity index (D) = Mₘ/Mₙ. *c*Data taken from Table 2, entry 5.
**Fig. S1** FT-IR spectra of monomers (A) 1a and (B) 2b and their polymer (C) \( P_{1a2b} \)

**Fig. S2** FT-IR spectra of monomers (A) 1a and (B) 2c and their polymer (C) \( P_{1a2c} \)
Fig. S4: H NMR spectra of monomer (A) 1a and (B) 2b and their polymer (C) P1a2b in CDCl₃. The solvent peaks are marked with asterisks.

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

**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.
**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.

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Fig. S11 ¹H NMR spectra of P1b2b in CDCl₃: (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.