

# Three Component Reactions for Post-Polymerization Modifications.

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SUPPORTING INFORMATION

## Experimental Section

**Materials.** The 4-toluene sulfonyl azide (toluene solution, 11 ~ 15 wt %), 1-aza-15-crown-5-ether, CuI, and CuBr(PPh<sub>3</sub>)<sub>3</sub> were available from the Sigma-Aldrich Chemicals Co., and used as received. The pentafluorophenyl-4-vinylbenzoate was synthesized according to a previous report.<sup>1</sup> Although a dipeptide, MeO-Leu-Pro-NH, is commercially available from Ambinter, the synthetic procedure was also reported by Rydzewski et al.<sup>2</sup> 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from diethylether. All other chemicals were commercially available and used without further purification unless otherwise stated.

**Instruments.** All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deuterated solvents and chemical shifts (δ) were given in ppm as solvent peak as internal standard. <sup>19</sup>F NMR spectra were recorded on a Bruker 188 MHz FT-NMR spectrometer in deuterated solvents. The size exclusion chromatography (SEC) was performed at room temperature in THF at a flow rate of 1.0 mL·min<sup>-1</sup>. The number-average molecular weight (*M<sub>n</sub>*) and polydispersity (*M<sub>w</sub>*/*M<sub>n</sub>*) of the polymers were calculated on the basis of a polystyrene calibration. Mass spectroscopy was measured by using Agilent 6224 ESI-TOF.

### Synthesis of an acetylene functionalized polymer.

**Synthesis of pentafluorophenyl ester functionalized random copolymer (P(S<sub>0.8</sub>-co-PFP<sub>0.2</sub>)).** A dry 1,4-dioxane solution (25 mL) containing pentafluorophenyl 4-vinylbenzoate (8.0 g, 25.5 mmol), styrene (10.7 g, 103 mmol) and AIBN (210 mg, 1.28 mmol) was degassed with Ar at r.t. for 10 minutes. After degassing, the reaction mixture was stirred at 80 °C for 17 hours. The reaction mixture was then cooled down and exposed to air to quench the polymerization. The polymer was purified by reprecipitation (THF/MeOH) to produce white solid. Yield, 17.4 g (93.2 %). SEC (THF); *M<sub>n</sub>* = 24,000, PDI = 1.9

**Synthesis of acetylene functionalized random copolymer (P(S<sub>0.8</sub>-co-C≡C<sub>0.2</sub>)).** To a THF solution (50 mL) containing P(S<sub>0.8</sub>-co-PFP<sub>0.2</sub>) (16.0 g, [PFP-ester]<sub>0</sub> = 23.8 mmol), propargylamine (3.93 g, 71.4 mmol) was added at r.t.. After stirring for 16 hours at room temperature, THF was evaporated under

vacuum condition. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (600 mL) and washed with  $1 \text{ mol}\cdot\text{L}^{-1} \text{HCl}_{\text{aq}}$  twice and  $1 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{CO}_{3\text{aq}}$  twice. The combined organic layer was dried over  $\text{MgSO}_4$  and evaporated. The residue was dissolved in a small portion of THF and poured into a large portion of hexane to afford a white powder. Yield, 9.22 g (93.2 %). SEC (THF);  $M_n = 24,000$ , PDI = 1.8

### Synthesis of model compounds.

**Synthesis of *N*-(prop-2-ynyl)-4-vinylbenzamide.** To a THF solution (5.0 mL) of pentafluorophenyl 4-vinylbenzoate (5.0 g, 16.0 mmol) and  $\text{NEt}_3$  (3.5 ml, 24.0 mmol), propargylamine (1.3 g, 24.0 mmol) was slowly added at room temperature and allowed to react for 23 hours. Afterwards the reaction mixture filtered and the filtrate was evaporated under vacuum. The residue was dissolved in diethylether (200 mL) and washed with  $1 \text{ mol}\cdot\text{L}^{-1} \text{HCl}_{\text{aq}}$  (100 mL x 2) and  $1 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{CO}_{3, \text{aq}}$  (200 mL x 2). The combined organic layer was dried over  $\text{MgSO}_4$  and evaporated to yield *N*-(prop-2-ynyl)-4-vinylbenzamide as a pale yellow solid.

Yield, 2.47 g (13.3 mmol, 83.3 %)  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.76 (d,  $J = 8.3$  Hz, 2H), 7.45 (d,  $J = 8.0$  Hz, 1H), 6.73 (dd,  $J = 17.6, 10.9$  Hz, 1H), 5.86 (d,  $J = 0.8$  Hz, 1H), 5.38 (d,  $J = 0.8$  Hz, 1H), 4.25 (dd,  $J = 5.2, 2.6$  Hz, 2H), 2.28 (t,  $J = 2.5$  Hz, 1H).

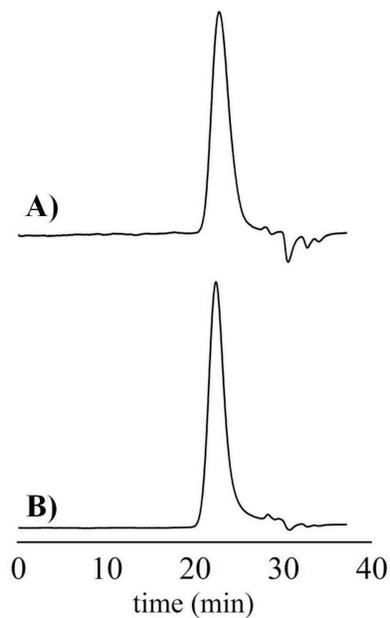
**Synthesis of *N*<sup>1</sup>,*N*<sup>1</sup>-di(*n*-hexyl)-*N*<sup>2</sup>-(4-methylbenzenesulfonyl)-2-(4-vinylphenyl)acetamidine (St-NSA).** Under Ar atmosphere at room temperature, degassed 2.95 g of 4-toluenesulfonyl azide toluene solution (11 ~ 15 wt %, 383 mg, 1.94 mmol) was slowly added to a THF solution (4.0 mL) of *N*-(prop-2-ynyl)-4-vinylbenzamide (300 mg, 1.62 mmol), dihexylamine (360 mg, 1.94 mmol), and CuI (30.5 mg, 0.16 mmol). After the reaction mixture was stirred for 18 hours, the reaction mixture was diluted with THF and passed through aluminiumoxide. The filtrate was evaporated under vacuum and the residue was purified by column chromatography (silica gel, eluent; EtOAc/hexane = 2/5) to yield St-NSA as a pale yellow solid.

Yield, 450 mg (0.83 mmol, 51.2 %)  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.83 (d,  $J = 8.3$  Hz, 2H), 7.76 (d,  $J = 8.2$  Hz, 2H), 7.44 (d,  $J = 8.3$  Hz, 2H), 7.23 (d,  $J = 8.5$  Hz, 2H), 6.75 (dd,  $J = 17.6, 10.9$  Hz,

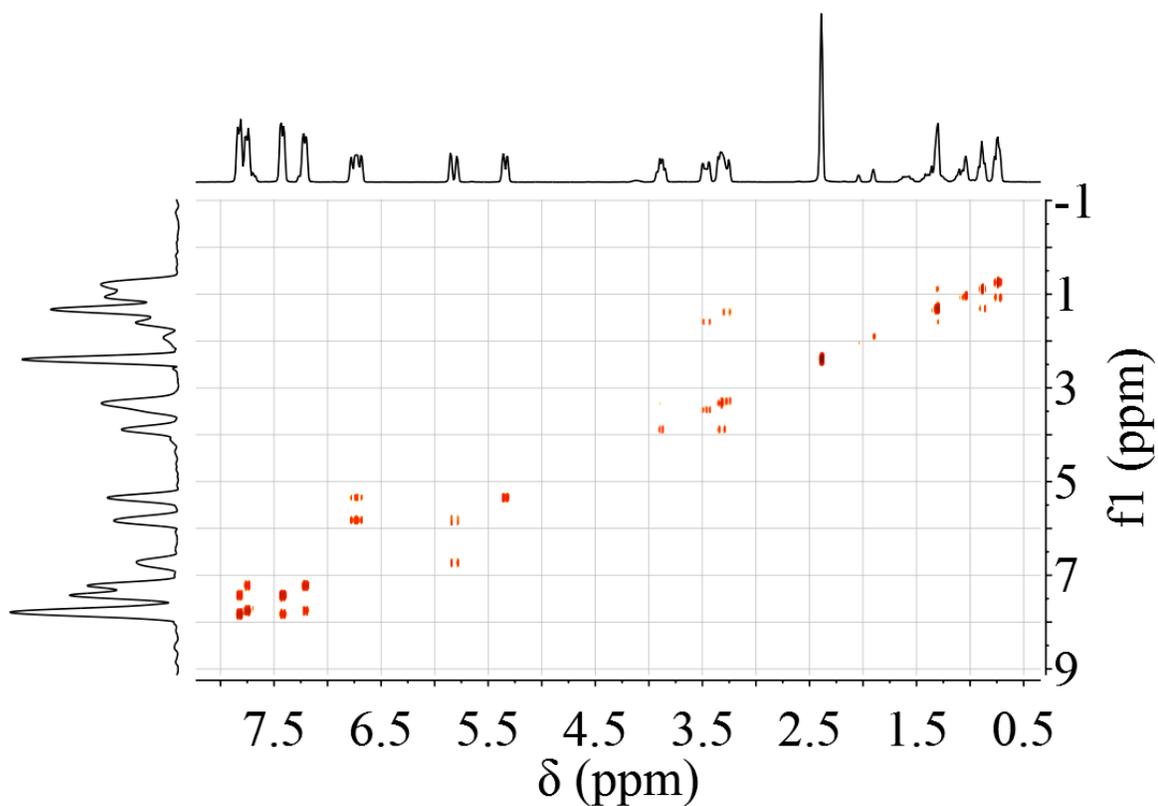
1H), 5.86 (d,  $J = 0.8$  Hz, 1H), 5.35 (d,  $J = 11.6$  Hz, 1H), 3.95 – 3.83 (m, 2H), 3.51 – 3.43 (m, 2H), 3.38 – 3.22 (m, 4H), 2.40 (s, 3H), 1.67 – 1.22 (m, 10H), 1.16 – 0.99 (m, 6H), 0.95 – 0.71 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm):  $\delta$  167.25, 164.31, 141.88, 141.17, 140.54, 136.04, 133.01, 129.02, 127.49, 126.18, 125.91, 115.73, 77.50, 77.28, 77.08, 76.65, 49.46, 49.12, 36.89, 31.44, 31.26, 31.10, 28.98, 26.50, 26.46, 26.42, 22.52, 22.33, 21.42, 17.58, 13.99, 13.95. ESI-MS; Calcd for  $\text{C}_{31}\text{H}_{46}\text{N}_3\text{O}_3\text{S}$ ,  $[\text{M}+\text{H}^+]$ ; 540.33; Found for  $[\text{M}+\text{H}^+]$ ; 540.3473.

**Synthesis of model copolymer ( $\text{P}(\text{S}_{0.8}\text{-co-NSA}_{0.2})$ ).** A dry 1,4-dioxane solution (0.5 mL) containing St-NSA (150 mg, 0.28 mmol), styrene (116 mg, 1.11 mmol) and AIBN (2.1 mg, 0.013 mmol) was degassed with Ar at r.t. for 10 minutes. After degassing, the reaction mixture was stirred at 80 °C for 16 hours. The reaction mixture was then cooled down and exposed to air to quench the polymerization. The polymer was purified by reprecipitation (THF/MeOH) to yield a white solid. Yield, 121 mg (45.5 %). SEC (THF);  $M_n = 29,000$ , PDI = 1.9

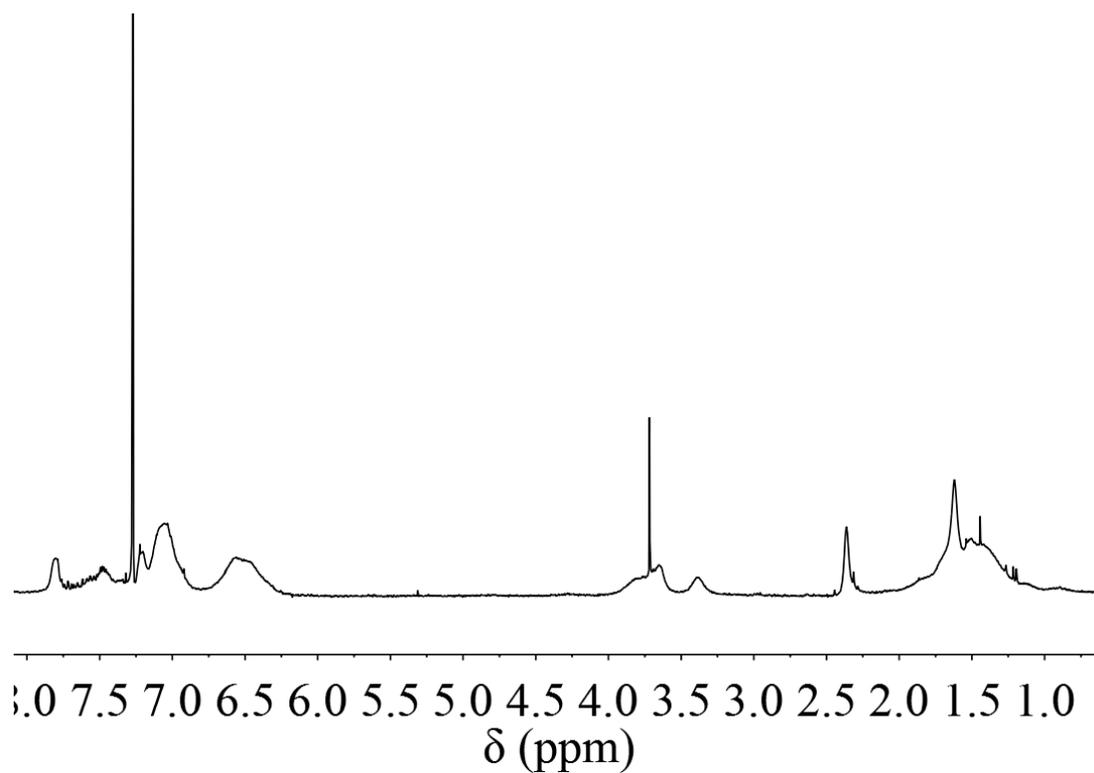
**CuMCR based post-modification reactions on polymers.** A typical post-modification reaction based on Cu catalyzed three component reaction was carried out as follows: To a THF solution (1.0 mL) of  $\text{P}(\text{S}_{0.8}\text{-co-C}\equiv\text{CH}_{0.8})$  (100 mg,  $[\text{C}\equiv\text{CH}]_0 = 0.175$  mmol) and  $\text{CuBr}(\text{PPh}_3)_3$  (32.6 mg, 0.035 mmol), toluene solution (1.5 mL) of diisopropylethylamine (9.0 mg, 0.070 mmol) and dihexylamine (125 mg, 0.70 mmol) was combined under Ar atmosphere. After stirring at room temperature for 5 minutes, toluene solution (0.5 mL) of 4-toluenesulfonyl azide (69.0 mg, 530 mg of 11 ~ 15 wt % toluene solution, 0.32 mmol) was dropwise added at room temperature for 10 minutes under Ar atmosphere. After the reaction mixture was stirred for 4 hours, the reaction mixture was diluted with THF and passed through aluminiumoxide. The filtrate was evaporated under vacuum. The polymer was purified by reprecipitation (THF/MeOH or  $\text{Et}_2\text{O}$ ) to yield a pale yellowish powder. Yield; 124 mg (77.0 %).



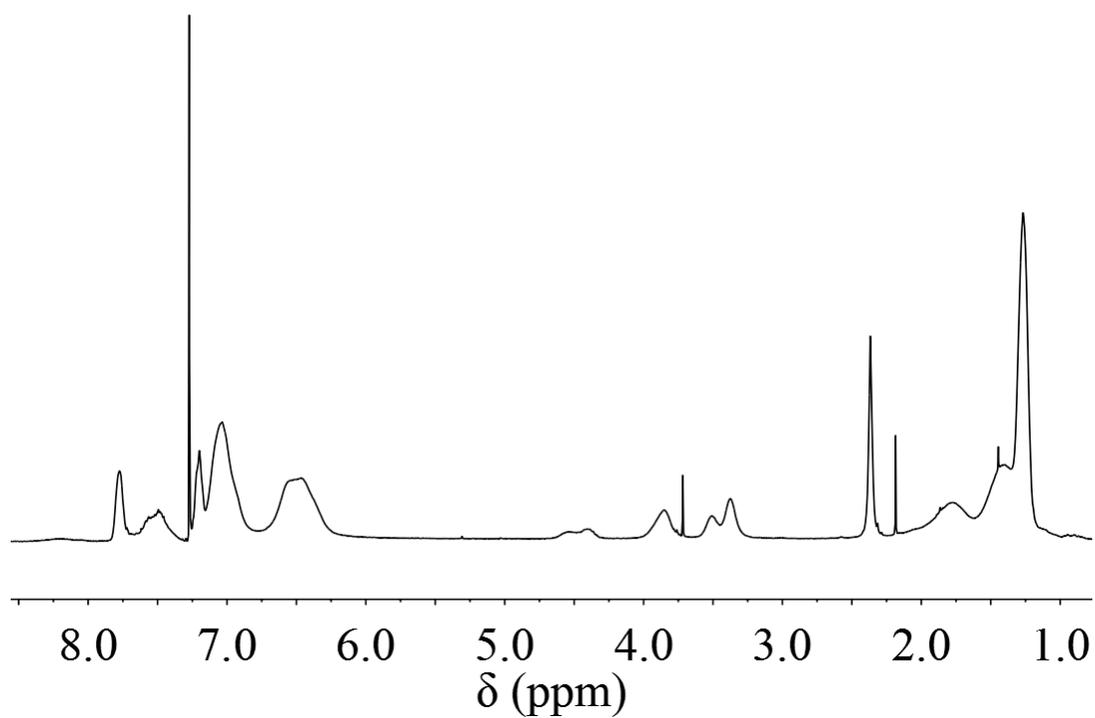
**Figure S-1.** SEC traces of  $P(S_{0.8}\text{-}co\text{-}C\equiv CH_{0.2})$  (**A**) and the obtained polymer (**B**, Table 1, run 1) measured in THF.



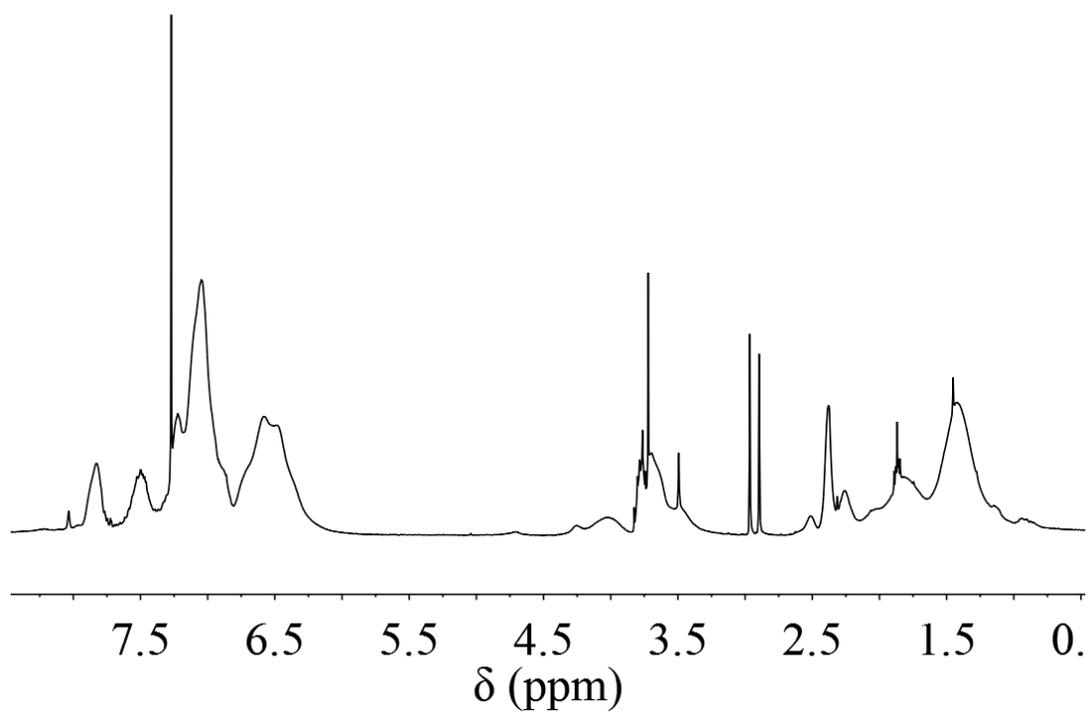
**Figure S-2.**  $^1H$ - $^1H$  COSY NMR spectrum of St-NSA in  $CDCl_3$ .



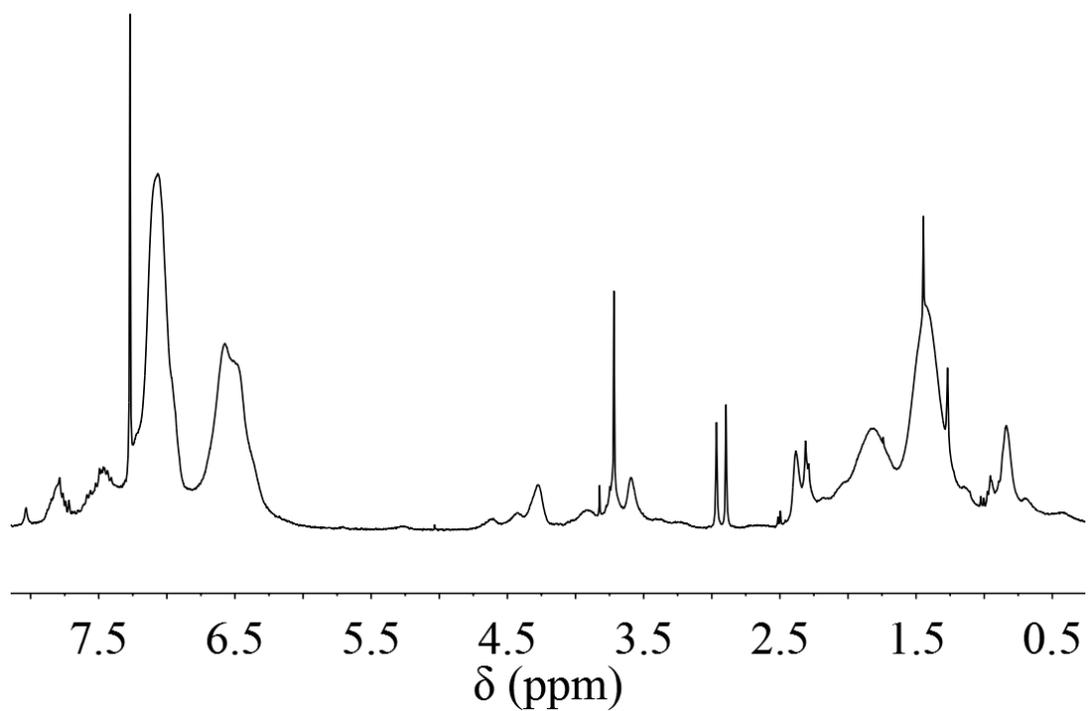
**Figure S-3.** <sup>1</sup>H NMR spectrum of the obtained polymer (Table 1, run 4) in CDCl<sub>3</sub>.



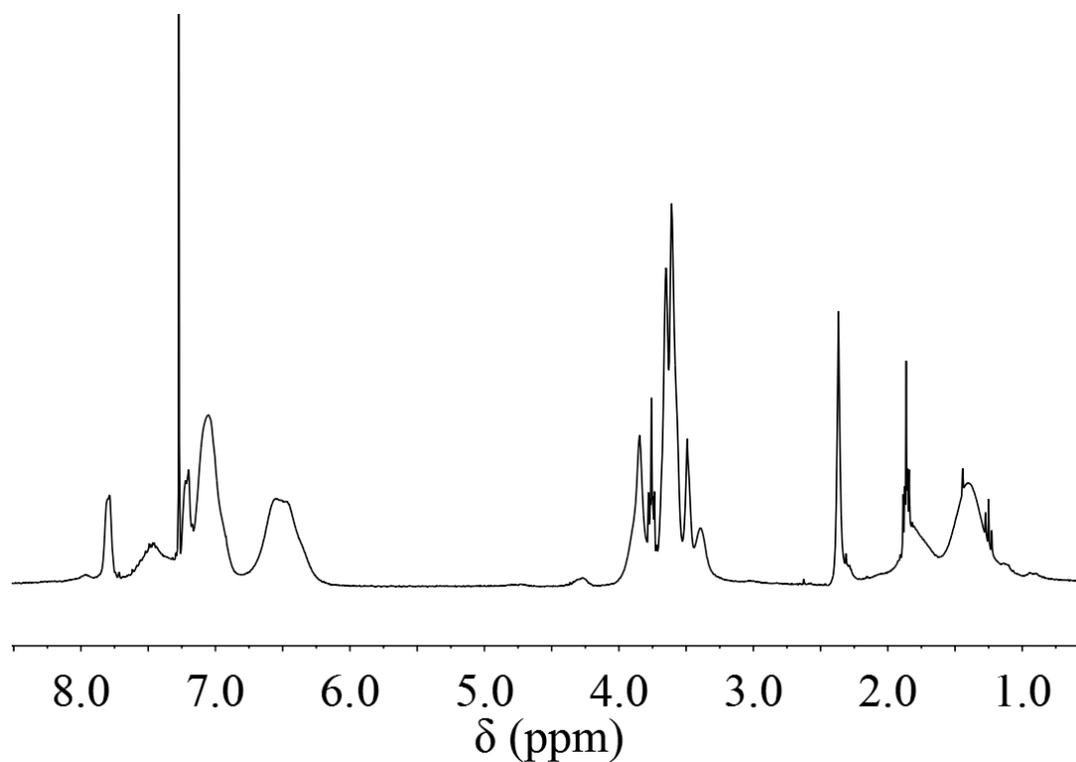
**Figure S-4.** <sup>1</sup>H NMR spectrum of the obtained polymer (Table 1, run 5) in CDCl<sub>3</sub>.



**Figure S-5.**  $^1\text{H}$  NMR spectrum of the obtained polymer (Table 1, run 6) in  $\text{CDCl}_3$ .



**Figure S-6.**  $^1\text{H}$  NMR spectrum of the obtained polymer (Table 1, run 7) in  $\text{CDCl}_3$ .



**Figure S-7.**  $^1\text{H}$  NMR spectrum of the obtained polymer (Table run 8) in  $\text{CDCl}_3$ .

**References;**

1. Nilles, K.; Theato, P., *Eur. Polym. J.* **2007**, *43* (7), 2901-2912.
2. Rydzewski, R. M.; Bryant, C.; Oballa, R.; Wesolowski, G.; Rodan, S. B.; Bass, K. E.; Wong, D. H., *Bioorgan. Med. Chem.* **2002**, *10* (10), 3277-3284.