

## Electronic Supplementary Information

### **Ionic polyacetylene with unique nanostructure and high stability by metathesis cyclopolymerization-induced self-assembly**

Hongfei Li<sup>a,b</sup>, Wei Song<sup>c,\*</sup>, Xiaojuan Liao<sup>a</sup>, Ruyi Sun<sup>a</sup> and Meiran Xie<sup>a,\*</sup>

<sup>a</sup>*School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, China. E-mail: mrxie@chem.ecnu.edu.cn*

<sup>b</sup>*Department of Polymer Science and Engineering, Shanghai Key Laboratory of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, Shanghai 200240, China*

<sup>c</sup>*Department of Polymer and Composite Material, School of Materials Engineering, Yancheng Institute of Technology, Yancheng, 224051, China. E-mail: sw121092@ycit.cn*

*Synthesis of 2-(dimethylamino)ethyl 2-(prop-2-ynyl)pent-4-ynoate (1)*

To a solution of *N,N*-dimethylethanolamine (1.9 g, 21.0 mmol), EDCI (3.2 g, 17.0 mmol), and DMAP (366.0 mg, 3.0 mmol) in fresh distilled DCM (10 mL), the solution of 2-(2-propynyl)-4-pentynoic acid (1.9 g, 14.0 mmol) in fresh distilled DCM (10 mL) was added dropwise under nitrogen at 0 °C, and the mixture was warmed to room temperature and stirred for 12 h. The resulting mixture was diluted with DCM (20 mL) and then washed with saturated NaHCO<sub>3</sub> aqueous solution, water, and saturated brine. Then, dried over anhydrous MgSO<sub>4</sub>. After removal of solvent, the crude product was purified using column chromatography (ethyl acetate/petroleum ether = 1:1) to yield intermediate compound **1** as a pale yellow liquid (2.2 g, 11.0 mmol, 78%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 4.26 (t, 2H, COOCH<sub>2</sub>CH<sub>2</sub>), 2.86 (m, 1H, (CH<sub>2</sub>)<sub>2</sub>CH), 2.70-2.56 (m, 6H, CH≡CCH<sub>2</sub> + CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 2.30 (s, 6H, -N(CH<sub>3</sub>)<sub>2</sub>), 2.08 (s, 2H, CH≡CCH<sub>2</sub>). IR (KBr): 3281 (-NH-), 3121 (C≡CH), 2119 (C≡C), 1737 (C=O) cm<sup>-1</sup>. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>, ppm): δ -78.80 (TFSI).

*Synthesis of ionized 2-(dimethylamino)ethyl 2-(prop-2-ynyl)pent-4-ynoate (M2)*

To a solution of 2-(dimethylamino)ethyl-2-(prop-2-ynyl)pent-4-ynoate (**1**) (2.2 g, 11.0 mmol) in CHCl<sub>3</sub> (10 mL), CH<sub>3</sub>I (6.0 g, 42.0 mmol) was added, and the mixture was stirred at 45 °C for 3 d. The mixture was concentrated and precipitated three times in diethyl ether and dried in vacuum to get iodized 2-(dimethylamino)ethyl-2-(prop-2-ynyl)pent-4-ynoate (**2**) as a white solid (3.4 g, 10.0 mmol, 92%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 4.70 (s, 2H, CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 4.23 (d, 2H, COOCH<sub>2</sub>CH<sub>2</sub>), 3.62 (d, 9H, N(CH<sub>3</sub>)<sub>3</sub>), 2.87 (m, 1H, (CH<sub>2</sub>)<sub>2</sub>CH), 2.83-2.56 (m, 4H, CH≡CCH<sub>2</sub>), 2.09 (m, 2H, CH≡CCH<sub>2</sub>).

To a solution of **2** (3.4 g, 10.0 mmol) in the mixed solvent of deionized water (10 mL), acetone (15 mL), and methanol (10 mL), LiTFSI (4.3 g, 15.0 mmol) in deionized water (10 mL) was added, and the mixture was stirred at room temperature for 2 d. The mixture

was concentrated and precipitated three times in diethyl ether and dried in vacuum to get **M2** as colorless viscous liquid (4.0 g, 8.0 mmol, 80%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.60 (s, 2H,  $\text{CH}_2\text{N}(\text{CH}_3)_2$ ), 3.80 (d, 2H,  $\text{COOCH}_2\text{CH}_2$ ), 3.27 (t, 9H,  $\text{N}(\text{CH}_3)_3$ ), 2.90 (m, 1H,  $(\text{CH}_2)_2\text{CH}$ ), 2.77-2.56 (m, 4H,  $\text{CH}\equiv\text{CCH}_2$ ), 2.24 (s, 2H,  $\text{CH}\equiv\text{CCH}_2$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.82, 119.76, 80.31, 71.39, 65.03, 58.31, 54.19, 53.43, 42.87, 30.94, 19.83.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -79.19. IR (KBr): 3304 ( $\text{C}\equiv\text{CH}$ ), 2121 ( $\text{C}\equiv\text{C}$ ), 1751 ( $\text{C}=\text{O}$ )  $\text{cm}^{-1}$ . HR-ESIMS: Calcd. For  $\text{C}_{13}\text{H}_{20}\text{NO}_2^+$  [**M2**] $^+$ : 222.1494, Found: 222.1484.

### *General procedure for polymerizations*

#### *Synthesis of homopolymer via MCP*

Homopolymer **P2** was prepared by MCP using **Ru-III** as the catalyst and a typical procedure was as follow. In a dry nitrogen-filled Schlenk tube, a solution of **Ru-III** (7.1 mg, 8  $\mu\text{mol}$ ) in 1 mL of THF, which was degassed in three freeze-vacuum-thaw cycles, was added to a degassed solution of **M2** (100.0 mg, 0.2 mmol) in 1 mL of THF to give a monomer concentration of 0.2  $\text{mol}\cdot\text{L}^{-1}$ . After 2 h, the polymerization was quenched by adding an excess of ethyl vinyl ether with stirring for 30 min, and then precipitated into a large quantity of diethyl ether. Polymer was dissolved in acetone, and precipitated once again from diethyl ether. The obtained polymer was dried in a vacuum oven at 40  $^\circ\text{C}$  to give **P2** as a purple black solid (98 mg, 98%).  $^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  6.92 (d, 2H,  $-\text{CH}=\text{CH}-$  on polymer chain), 4.77 (s, 2H,  $\text{CH}_2\text{N}(\text{CH}_3)_2$ ), 4.01 (s, 2H,  $\text{COOCH}_2\text{CH}_2$ ), 3.59-3.33 (m, 9H,  $\text{N}(\text{CH}_3)_3$ ), 3.27-2.99 (m, 5H,  $(\text{CH}_2)_2\text{CH} + (\text{CH}_2)_2\text{CH}$ ).  $^{13}\text{C}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  174.53, 138.35, 123.89, 123.36, 121.34, 118.79, 116.24, 65.04, 58.21, 53.79, 39.76, 36.46. IR (KBr): 3044 ( $\text{CH}=\text{CH}$ ), 1736 ( $\text{C}=\text{O}$ )  $\text{cm}^{-1}$ .

#### *Synthesis of random copolymer via MCP*

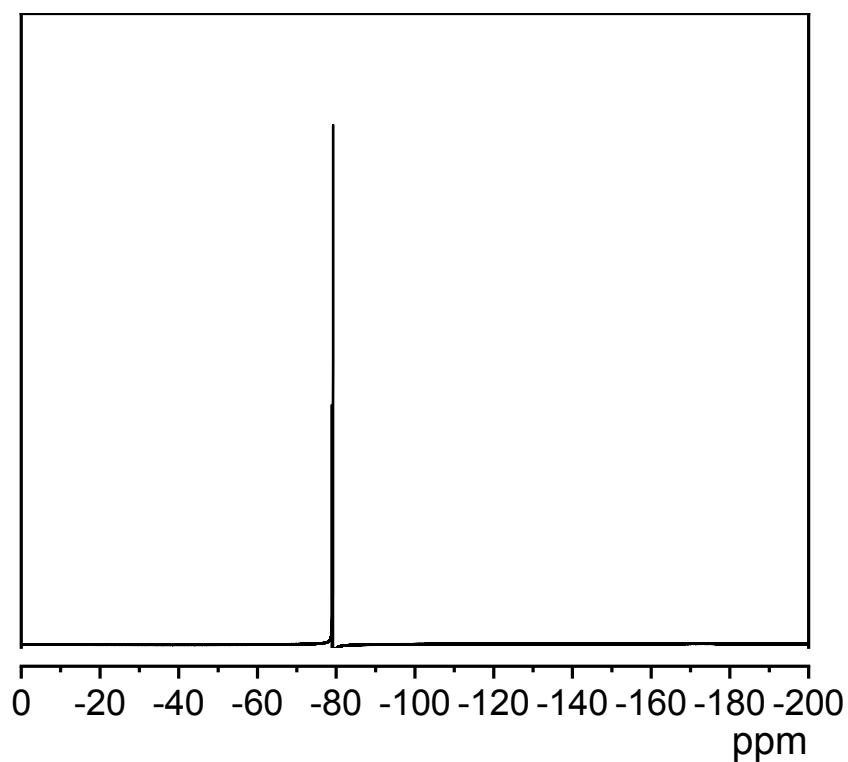
The random copolymers were prepared by MCP with the mixture solution of the two

monomers, and a typical procedure was as follow. In a nitrogen-filled Schlenk tube, a solution of **Ru-III** (1.8 mg, 2  $\mu$ mol) in 1 mL of THF, which was degassed in three freeze-vacuum-thaw cycles, was added to a degassed solution of **M1** (120 mg, 0.05 mmol) and **M2** (25 mg, 0.05 mmol) in 2 mL of THF to give a monomer concentration of 0.05 mol·L<sup>-1</sup>. After stirring for 2 h, the polymerization was quenched by adding a drop of ethyl vinyl ether with stirring for further 30 min, and the solution was then poured into an excess of diethyl ether. The polymer was redissolved in acetone again, and precipitated once again from diethyl ether. The precipitate was dried under vacuum for 24 h at 40 °C to obtain block copolymer **P(1<sub>25-co</sub>-2<sub>25</sub>)** as a purple black viscous solid (120 mg, 90%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.74 (d, triazolium-*H*), 4.90 (s, -N=N-NCH<sub>2</sub>CH<sub>2</sub>O-), 4.77 (s, CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 4.45 (s, -NCH<sub>3</sub>), 4.22 (d, CHCH<sub>2</sub>O-), 4.14-3.98 (m, -NCH<sub>2</sub>CH<sub>2</sub>O-), 3.84-3.43 (m, CH<sub>2</sub>CHCH<sub>2</sub> + CH<sub>2</sub>CH<sub>2</sub>O- + COOCH<sub>2</sub> + -N(CH<sub>3</sub>)<sub>3</sub> + -N(CH<sub>3</sub>)<sub>3</sub>CH<sub>2</sub>), 2.78-2.60 (m, CCH<sub>2</sub>CH), 1.13 (t, -OCH<sub>2</sub>CH<sub>3</sub>).

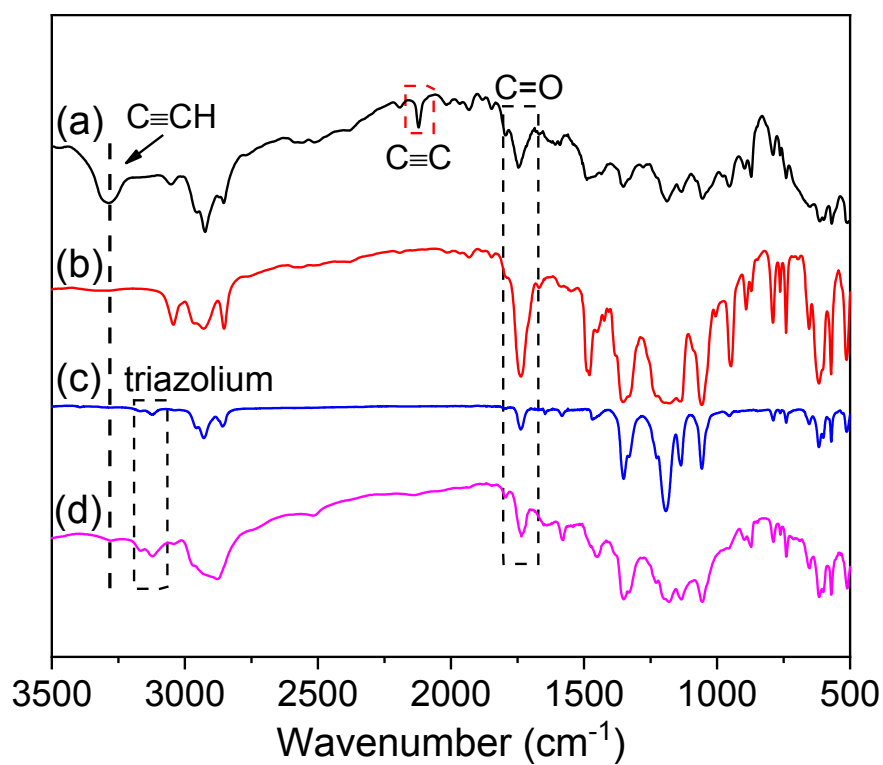
#### *Characterization of M2*

The structure of **M2** was characterized by NMR, HR-MS, and FT-IR spectroscopy. The <sup>1</sup>H NMR spectra of **1**, **2**, and **M2** were shown in Fig. 1a. The proton resonances of **1** at 4.26, 2.86, and 2.08 ppm were assigned to the methylene connected with ester group, methyne, and terminal acetylenic groups, respectively. The area ratios of these three peaks matched well with the predicted values of 2:1:2, indicating the correct structure of **1**. After ionization of **1** by CH<sub>3</sub>I and anion exchanging reaction from I<sup>-</sup> to TFSI<sup>-</sup>, the proton resonance of methylene connected with N atom shifted from 2.60 ppm to 4.70 ppm, and finally moved to 4.60 ppm. The changes of proton resonances in Fig. 1 demonstrated the successful synthesis of **M2**. In the <sup>13</sup>C NMR spectrum (Fig. 1b), the carbon resonances of carbonyl and acetylenic groups appeared at 171.82 and 70.31 ppm. In the <sup>19</sup>F NMR spectrum (Fig. S1†), fluorine resonance of TFSI<sup>-</sup> appeared at -79.90 ppm. In the FT-IR

spectrum of **M2** (Fig. S2a†), it was clear to see the acetylenic hydrogen stretching at 3304  $\text{cm}^{-1}$ , acetylenic carbon stretching at 2121  $\text{cm}^{-1}$ , and the ester group absorption peak appeared at 1751  $\text{cm}^{-1}$ . Finally, it was found that the molecular weight of  $[\mathbf{M2}]^+$  was 222.1484 by HR-ESIMS testing, which consistent with the theoretical calculation value of 222.1494. Apparently, all these points confirmed the successful preparation of **M2**.



**Fig. S1.**  $^{19}\text{F}$  NMR spectrum of **M2** in  $\text{CDCl}_3$ .



**Fig. S2.** FT-IR spectra of (a) **M2**, (b) **P2**, (c) **P1**, and (d) **P1-b-P2**.

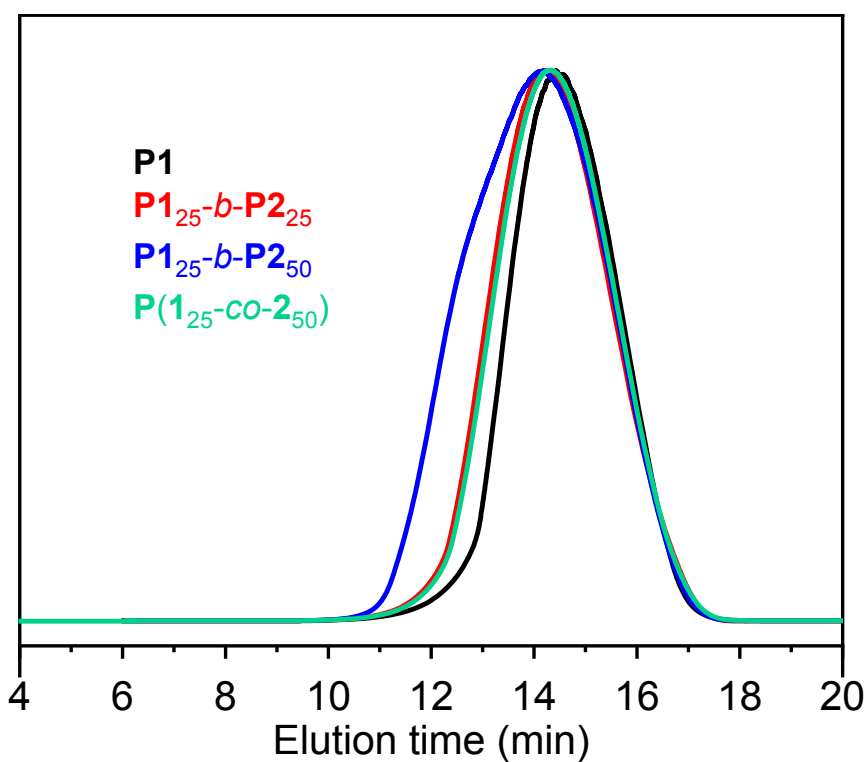
**Table S1**

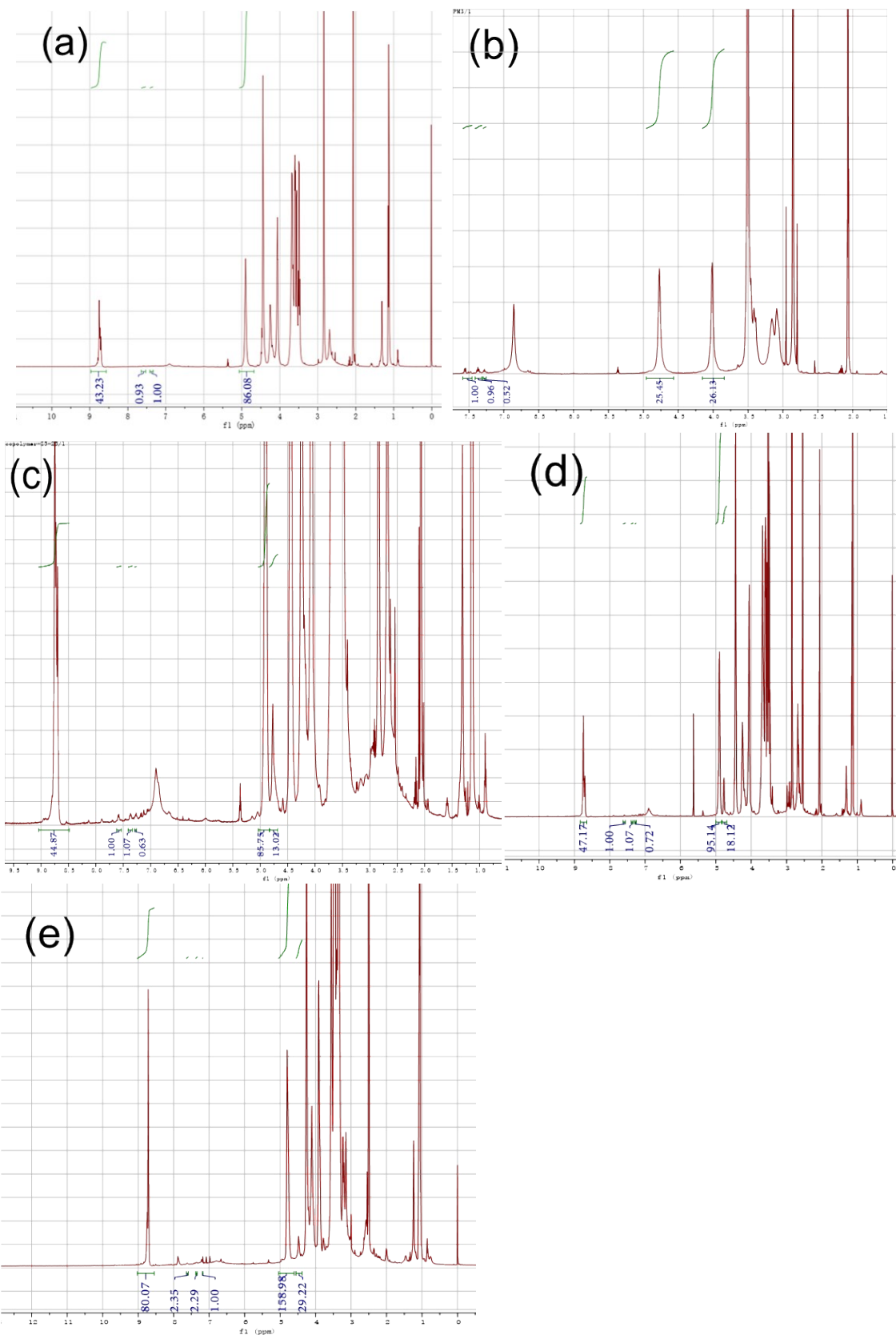
Solubility of polymers in various solvents at room temperature.

Run	Diethyl ether	CHCl <sub>3</sub>	THF	DMSO	Acetone
<b>P1</b>	–	++	++	++	++
<b>P2</b>	–	–	–	++	++
<b>P1-<i>b</i>-P2</b>	–	+–	+	++	++
<b>P(1<sub>25</sub>-<i>co</i>-2<sub>50</sub>)</b>	–	+–	+	++	++

\*1 mg of matter in 1 mL of solvent.

–: insoluble; +–: partially soluble; +: soluble; ++: good soluble.

**Fig. S3.** GPC traces of homopolymer and copolymers.



**Fig. S4.**  $^1\text{H}$  NMR spectra of (a) P1<sub>25</sub>, (b) P2<sub>25</sub> (c) P1<sub>25</sub>-b-P2<sub>25</sub>, (d) P1<sub>25</sub>-b-P2<sub>50</sub>, and (e) P(1<sub>25</sub>-co-2<sub>50</sub>).



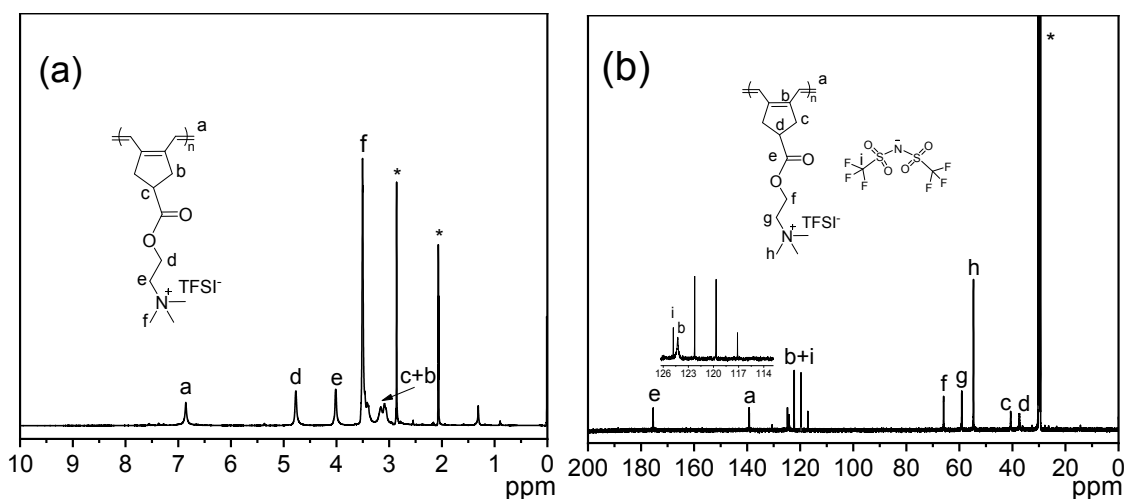


Fig. S5. (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectra of **P2** in  $(\text{CD}_3)_2\text{CO}$ .

Table S2

The composition of block copolymers by  $^1\text{H}$  NMR analysis.

	$^a\text{S}_i:\text{S}_n$	$^b\text{S}_i:\text{S}_n$
<b>P1<sub>25</sub>-b-P2<sub>25</sub></b>	2:1	4:1
<b>P1<sub>25</sub>-b-P2<sub>50</sub></b>	1:1	2:1

$^a$ Theoretical value of peak area ratio of  $\text{S}_i$  to  $\text{S}_n$ ;  $^b$ the actual value of peak area ratio of  $\text{S}_i$  to  $\text{S}_n$  calculated by  $^1\text{H}$  NMR analysis.

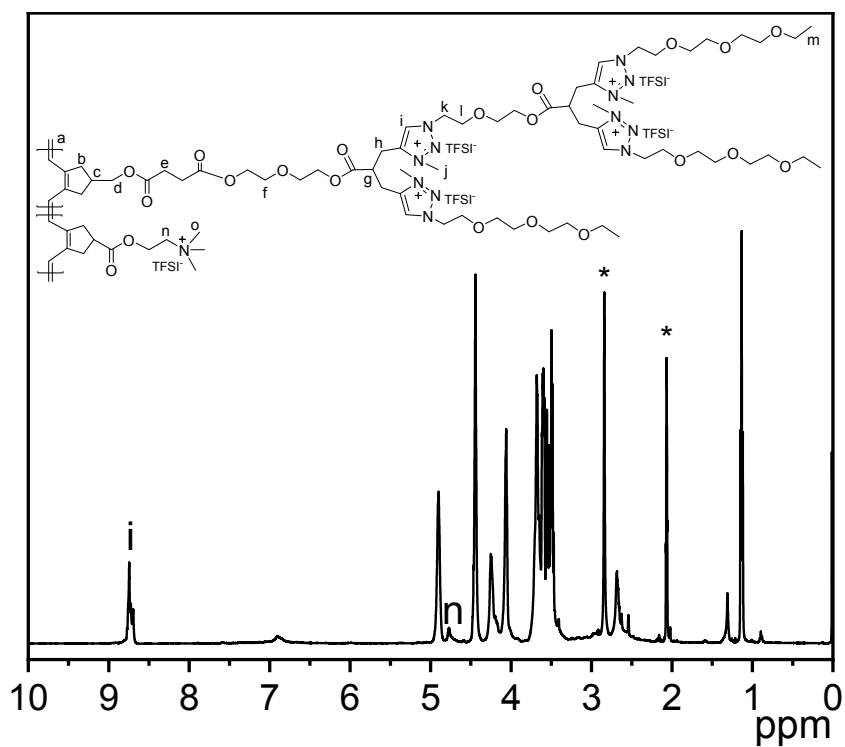


Fig. S6.  $^1\text{H}$  NMR spectrum of **P1<sub>25</sub>-b-P2<sub>50</sub>** in  $(\text{CD}_3)_2\text{CO}$ .

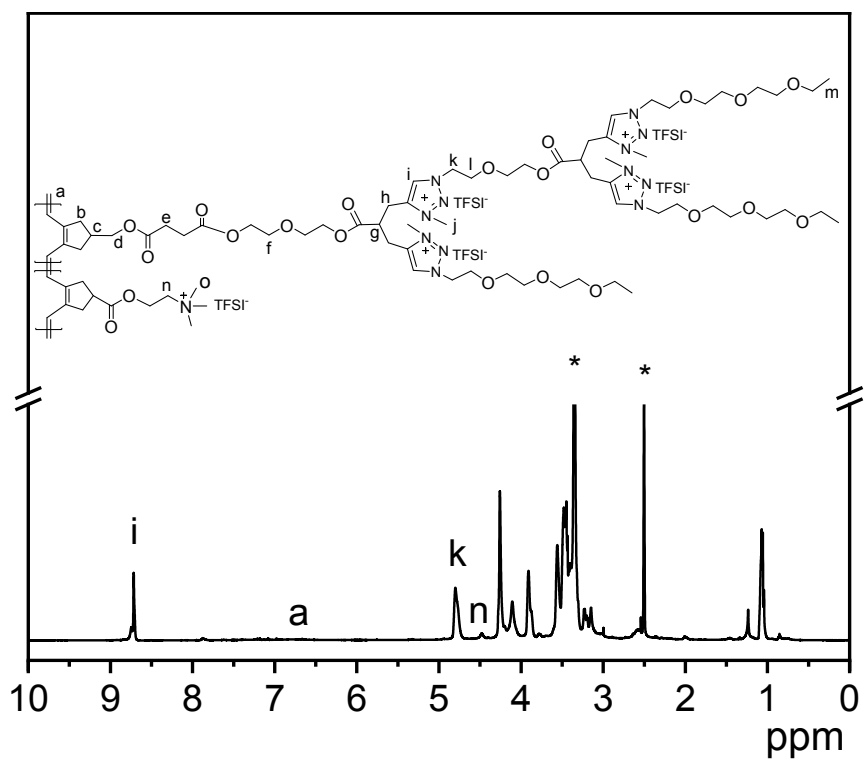
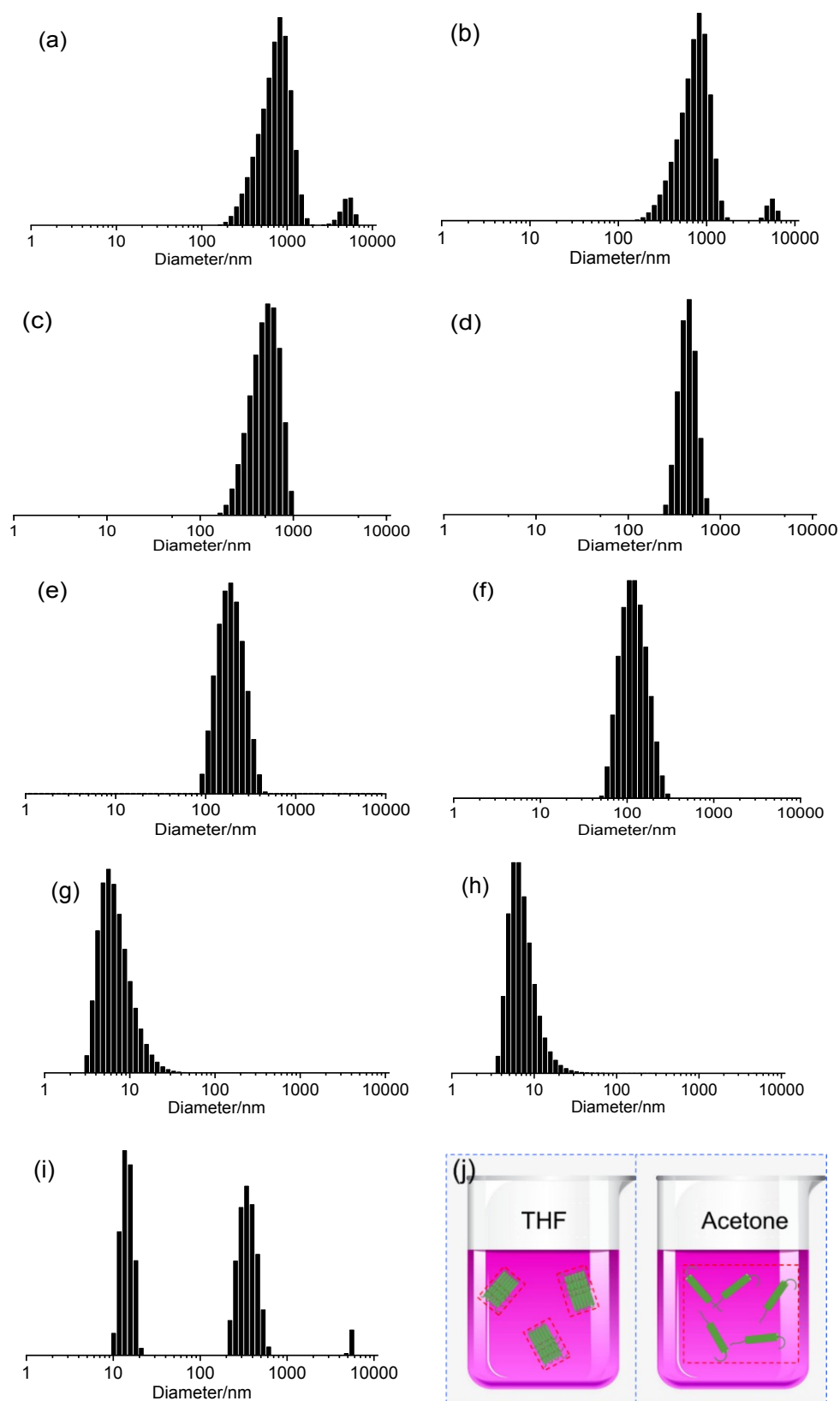
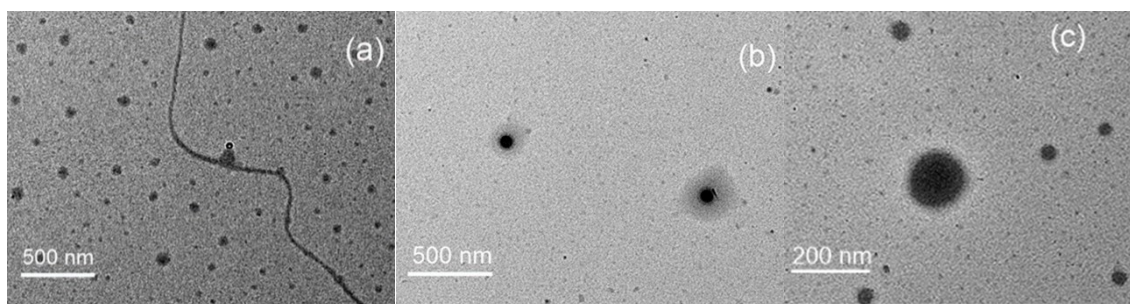


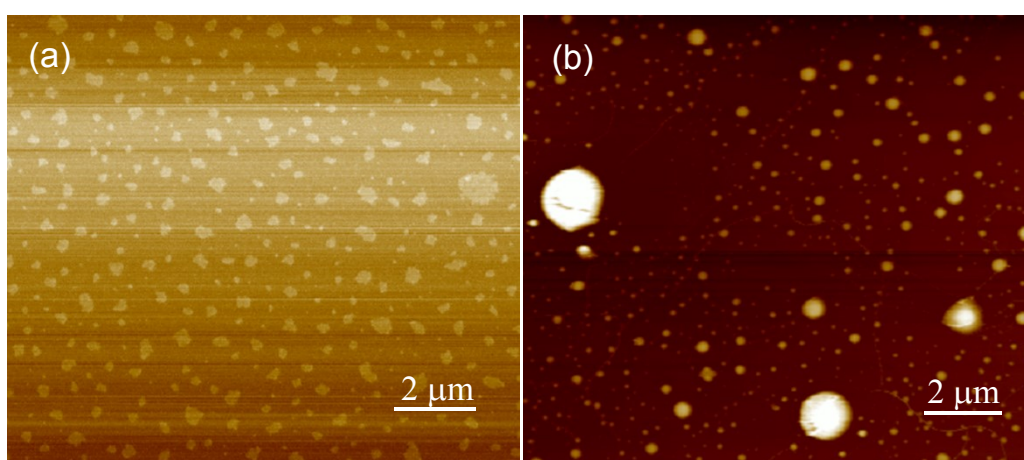
Fig. S7.  $^1\text{H}$  NMR spectrum of  $\text{P}(1_{25}\text{-co-}2_{25})$  in  $\text{DMSO-}d_6$ .



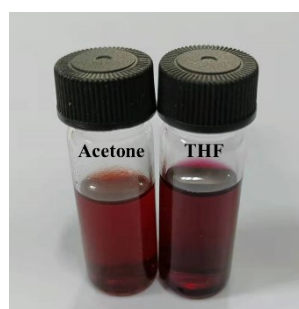
**Fig. S8.** Sizes of (a,c,e,g)  $P_{125}\text{-}b\text{-}P_{225}$  and (b,d,f,h)  $P_{125}\text{-}b\text{-}P_{250}$  at concentrations of (a,b) 1, (c,d) 0.1, and (e,f)  $0.05\text{ mg}\cdot\text{mL}^{-1}$  in THF, as well as (g,h)  $1\text{ mg}\cdot\text{mL}^{-1}$  in acetone; (i)  $P(125\text{-}co\text{-}225)$  at  $1\text{ mg}\cdot\text{mL}^{-1}$  in THF; (j) the schematic of block copolymers in different solvents.



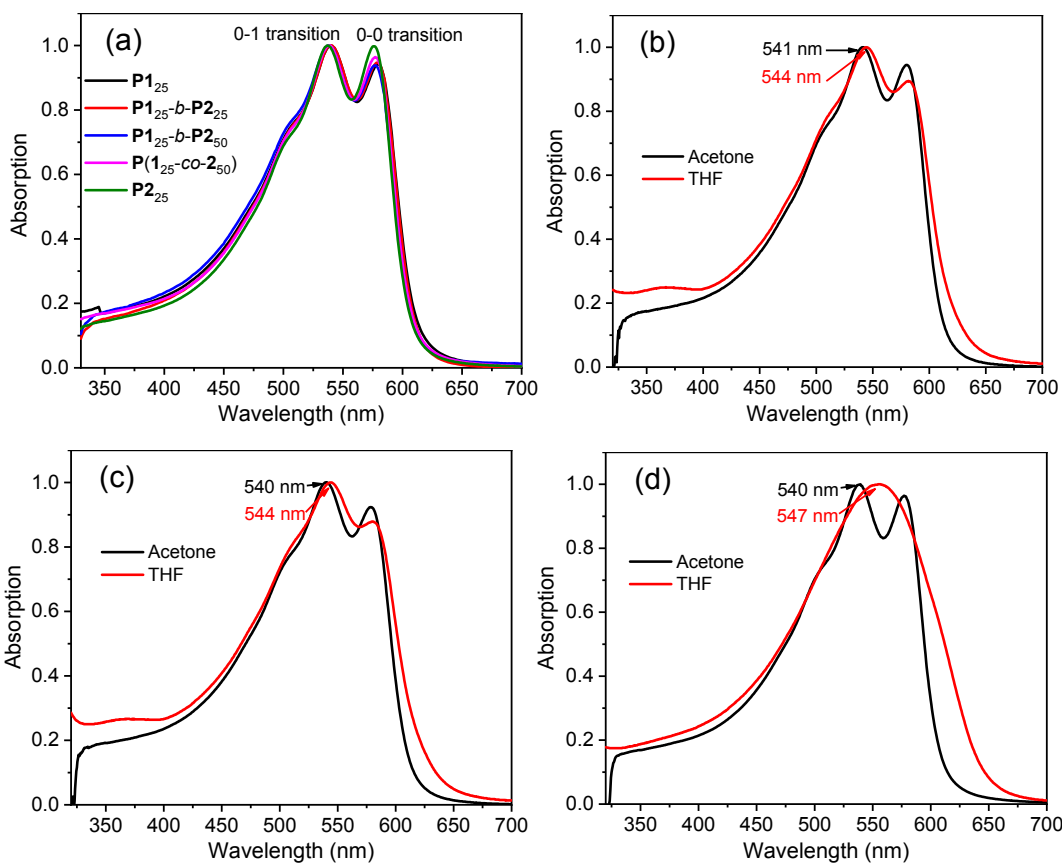
**Fig. S9.** TEM images of  $\mathbf{P1}_{25}\text{-}b\text{-}\mathbf{P2}_{25}$  in THF at the concentrations of (a)  $0.05 \text{ mg}\cdot\text{mL}^{-1}$  and (b)  $0.5 \text{ mg}\cdot\text{mL}^{-1}$ ; (c)  $\mathbf{P(1}_{25}\text{-}co\text{-}2_{50})$  in THF at a concentration of  $0.05 \text{ mg}\cdot\text{mL}^{-1}$ .



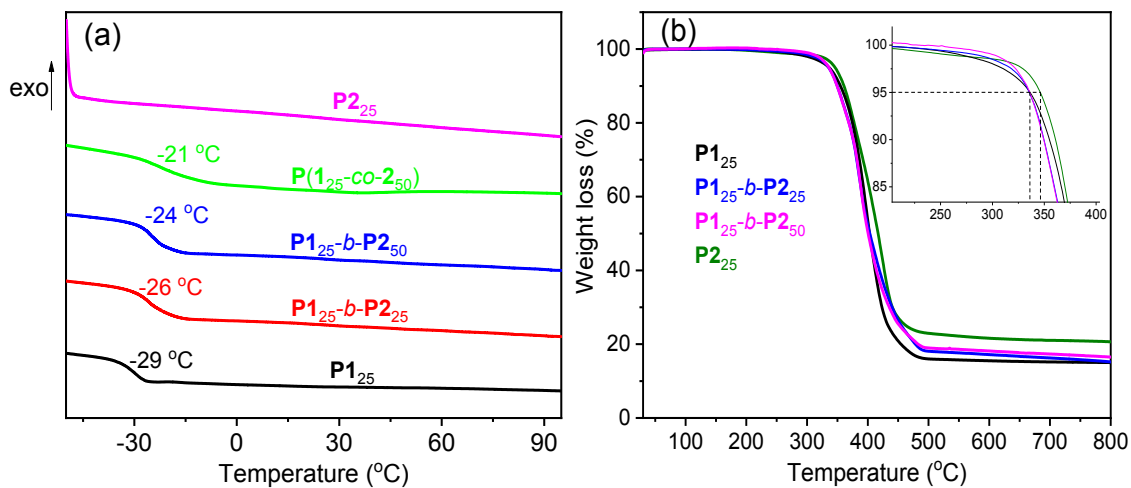
**Fig. S10.** AFM images of polymer thin films on mica substrate: (a)  $\mathbf{P1}_{25}\text{-}b\text{-}\mathbf{P2}_{50}$  prepared from acetone solution and (b)  $\mathbf{P1}_{25}\text{-}b\text{-}\mathbf{P2}_{25}$  prepared from THF solution at the same concentration of  $0.05 \text{ mg}\cdot\text{mL}^{-1}$ .



**Fig. S11.** Block copolymer  $\mathbf{P1}_{25}\text{-}b\text{-}\mathbf{P2}_{50}$  in acetone (left) and THF (right) solutions for 3 days at room temperature.



**Fig. S12.** (a) UV-vis spectra of homopolymers and copolymers in acetone; UV-vis spectra of (b)  $P_{125-b-P_{225}}$ , (c)  $P_{125-b-P_{250}}$ , and (d)  $P(1_{25-co-2_{25}})$  in acetone and THF.



**Fig. S13.** (a) DSC and (b) TGA curves of polymers.

## Notes and references

1. J. Wu, C. Wang, D. Zhou, X. Liao, M. Xie and R. Sun, *Macromol. Rapid Commun.*, 2016, **37**, 2017–2022.