

Supporting Information for

**Synthesis of triazole-dendronized polyacetylenes by metathesis
cyclopolymerization and the conductivity**

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MATERIALS

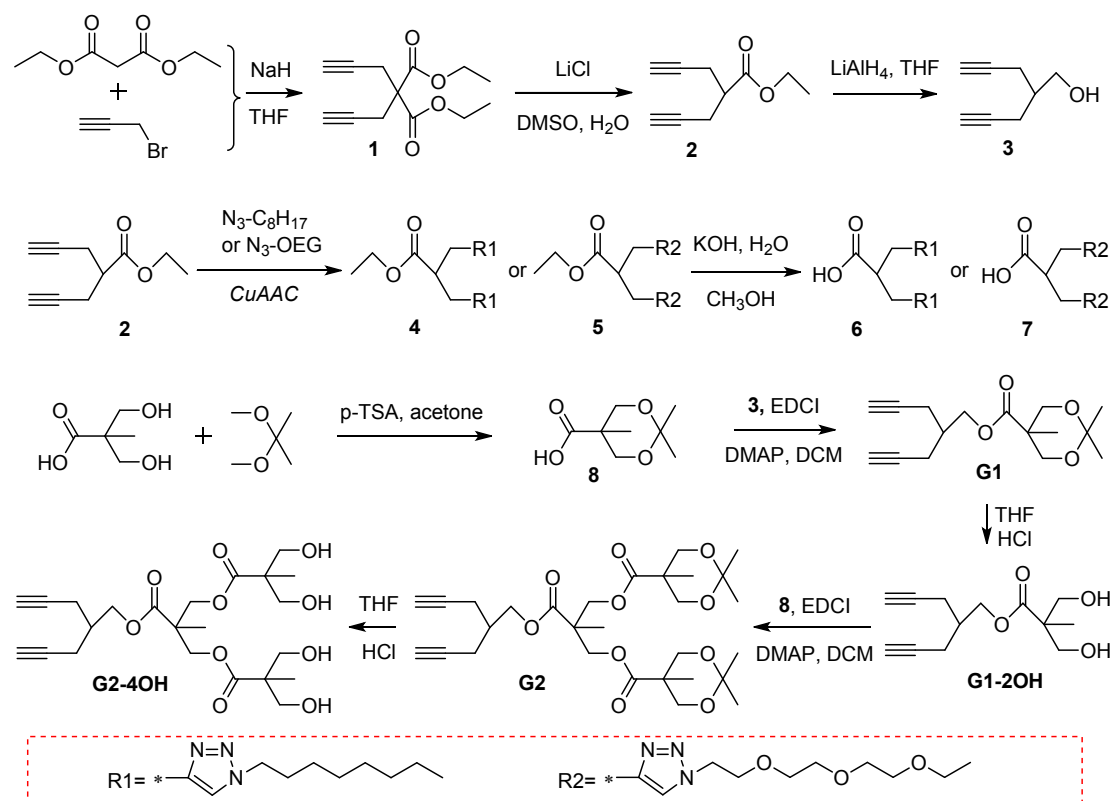
Diethyl malonate was purchased from Sinopharm Chemical Reagent Co., Ltd. Propargyl bromide was purchased from Shanghai Bangcheng Chemistry Co., Ltd. 2,2-Bis(hydroxymethyl) propionic, 2,2-dimethoxypropane, sodium hydride, and lithium aluminium hydride were purchased from J&K Scientific Co., Ltd. L-Ascorbic acid (99%), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99%), 4-Dimethylaminopyridine (DMAP, 98%), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI·HCl) were purchased from Shanghai Chemical Reagents Company. Solvents were used as received from commercial suppliers unless otherwise stated. Dichloromethane (DCM) was distilled from the drying agent of calcium hydride under nitrogen before use. Tetrahydrofuran (THF) was distilled from the drying agent of sodium/benzophenone under nitrogen. Chemicals of **1**,^{S1} **2**,^{S1} **3**,^{S1} **4**,^{S2} **5**,^{S2} **8**,^{S3} **G1**,^{S4} **G1-2OH**,^{S4} **G2**,^{S4} **G2-4OH**^{S4} were prepared according to literature procedures.

CHARACTERIZATION

^1H NMR (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on a Bruker DRX500 spectrometer with tetramethylsilane as an internal standard in CDCl_3 at room temperature. Gel permeation chromatography (GPC) for molecular weight and polydispersity index (PDI) analysis of freshly prepared polymers was performed on Malvern Viscotek GPCmax system with a refractive index detector, a 270 Dual Detector (light scattering and viscometer), and calculated by Malvern Viscotek OmniSec software. The column set was G+T6000M. Tetrahydrofuran (THF) was used as the eluting solvent with a flow rate of 1.0 mL/min at 35 °C, and polystyrene was used as the standard for calibration. Atomic force microscopy (AFM) observation was performed on an SPM AJ-III atomic force microscope at a measurement rate of

1.005 Hz in the tapping mode, and the AFM images were obtained at room temperature in air. Samples were prepared by drop coating of 0.005-0.05 mg/mL of a chloroform (CHCl_3) solution on a freshly cleaved mica plate, and were air-dried at room temperature.

EXPERIMENTAL PROCEDURES



Scheme S1. Syntheses of **3**, **6**, **7**, **G1-2OH**, and **G2-4OH**.

Synthesis of 6. KOH aqueous solution (0.5 mol in 20 mL of H₂O) was added dropwise to a solution of **4** (47.47 g, 0.1 mol) in CH₃OH (300 mL) under a nitrogen atmosphere in an ice-bath. The reaction mixture was heated to reflux at 80 °C for 32 h, concentrated under reduced pressure, and diluted with distilled water (50 mL). HCl aqueous solution (70 mL, 6 mol/L) was added dropwise to the mixture in an ice-bath, and the reaction solution had a pH of 1. It was extracted with DCM (4 × 100 mL). The organic layer was dried with Na₂SO₄, filtered and concentrated under reduced

pressure to give **6** as a pale yellow powder (43.34 g, 97%). ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.55 (s, triazole-*H*, 2H), 4.31 (t, J = 10.0 Hz, $\text{N}=\text{N}-\text{NCH}_2\text{CH}_2$, 4H), 3.21-3.03 (m, $\text{CHCH}_2\text{CN}=\text{N}-\text{N}$, 5H), 1.89 (t, J = 5.0 Hz, $\text{N}=\text{N}-\text{NCH}_2\text{CH}_2$, 4H), 1.31-1.26 (m, $\text{N}=\text{N}-\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 20H), 0.88 (t, J = 5.0 Hz, $\text{N}=\text{N}-\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 6H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 176.40, 144.57, 122.53, 50.51, 45.19, 31.71, 30.24, 29.05, 26.71, 26.49, 22.60, 14.08.

Synthesis of 7. KOH aqueous solution (90 mmol in 3 mL of H_2O) was added dropwise to a solution of **5** (10.27 g, 18 mmol) in CH_3OH (45 mL) under a nitrogen atmosphere in an ice-bath. The reaction mixture was heated to reflux at 80 °C for 1 d, concentrated under reduced pressure, and diluted with distilled water (30 mL). HCl aqueous solution (6 mL, 6 mol/L) was added dropwise to the mixture in an ice-bath, and the reaction solution had a pH of 7. It was extracted with DCM (3×100 mL). The organic layer was dried with Na_2SO_4 , filtered and concentrated under reduced pressure to give **7** as a yellow sticky liquid (8.20 g, 84%). ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.66 (s, triazole-*H*, 2H), 4.51 (t, J = 5.0 Hz, $\text{N}=\text{N}-\text{NCH}_2\text{CH}_2\text{O}$, 4H), 3.84 (t, J = 5.0 Hz, $\text{N}=\text{N}-\text{NCH}_2\text{CH}_2\text{O}$, 4H), 3.64-3.53 (m, $\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$, 20H), 3.20-3.01 (m, $\text{CHCH}_2\text{CN}=\text{N}-\text{N}$, 5H), 1.21 (t, J = 5.0 Hz, $\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$, 6H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 175.69, 144.72, 123.46, 70.62, 70.49, 69.68, 69.54, 66.64, 50.25, 45.33, 27.23, 14.99.

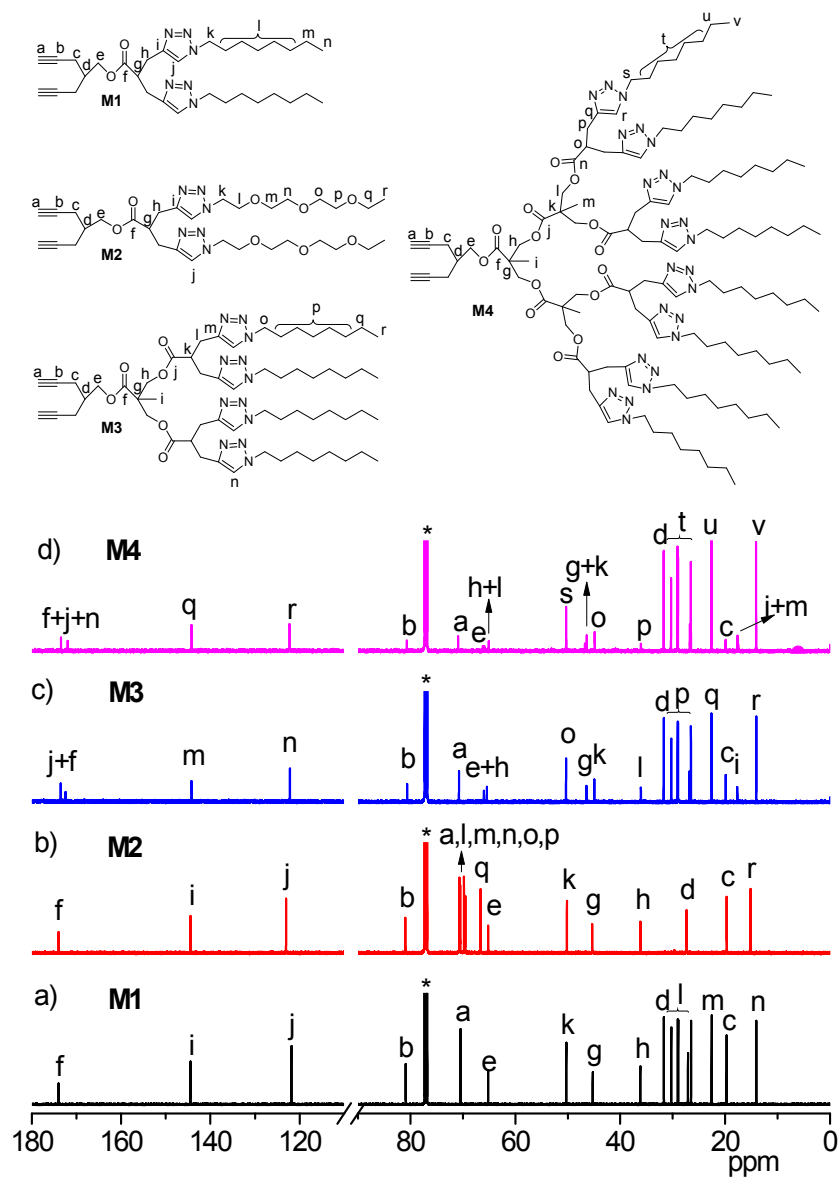


Fig. S1 ^{13}C NMR spectra of (a) **M1**, (b) **M2**, (c) **M3**, and (d) **M4** in CDCl_3 .

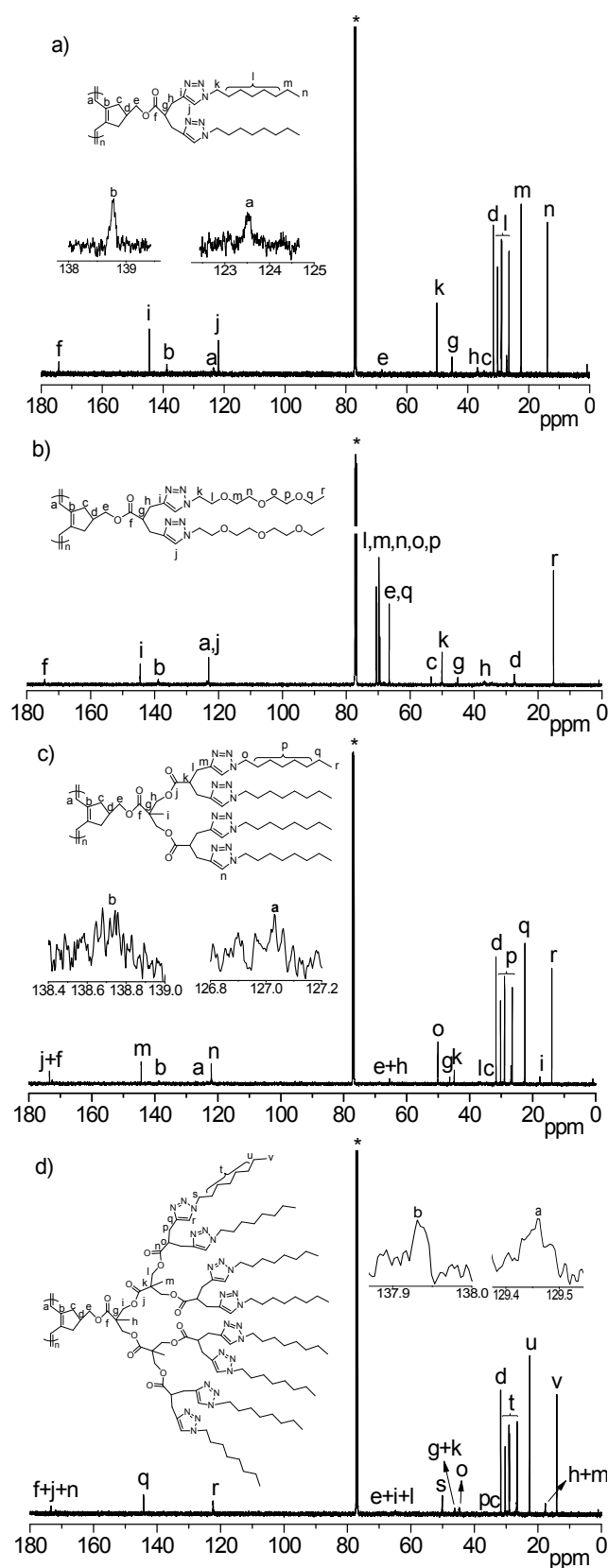


Fig. S2 ^{13}C NMR spectra of (a) poly(M1), (b) poly(M2), (c) poly(M3), and (d) poly(M4) in CDCl_3 .

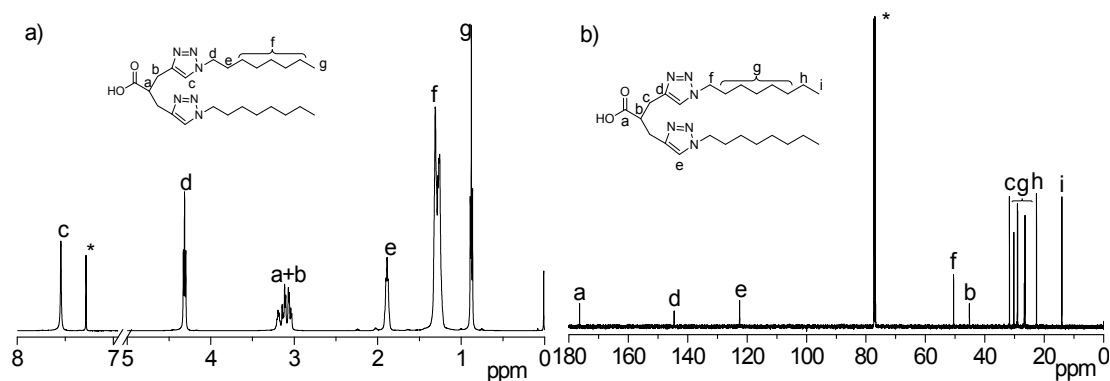


Fig. S3 ^1H NMR (a) and ^{13}C NMR (b) spectra of **6** in CDCl_3 .

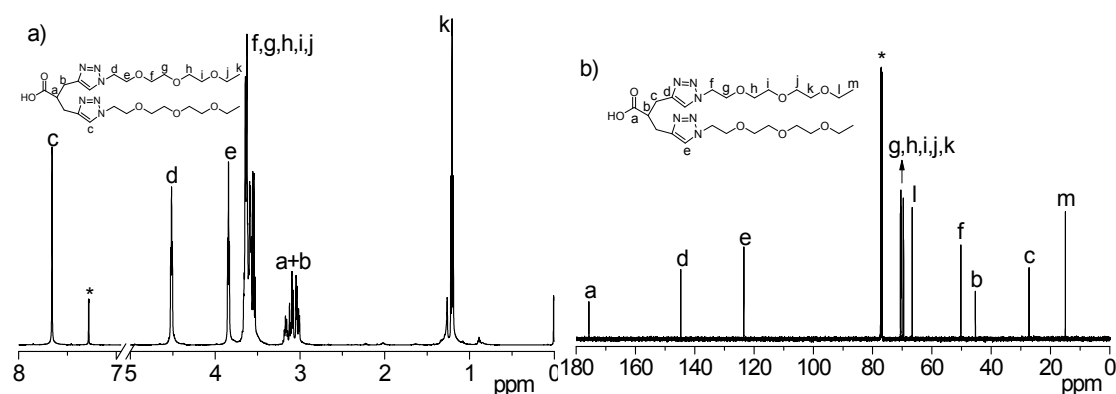


Fig. S4 ^1H NMR (a) and ^{13}C NMR (b) spectra of **7** in CDCl_3 .

Absolute Molecular Weights of Dendronized Polymers

It is known that dendronized polymers are hydrodynamically different from polystyrene,^{S5} and the π -conjugated polyene backbones are sensitive to air and moisture. Therefore, we prepared fresh polymer samples to measure their absolute molecular weights with light scattering detectors. Moreover, poly(**M4**) with larger bulky dendron units was taken as a representative example to discuss their absolute molecular weights and relative molecular weights (Table S1 and Fig. S5). It is obvious that the synthesized polymers had narrow PDIs, and their absolute molecular weights were almost two times higher than their corresponding relative molecular weights.

Table S1 Characteristics for polymerization of **M4** and the resultant polymers^a

Run	$[\text{M}]_0/[\text{Cat}]_0^b$	M_{n1}^c (kDa)	PDI_1^c	DP^d	M_{n2}^e (kDa)	PDI_2^e	Yield ^f (%)
1	25	34.1	1.07	15	18.0	1.06	81
2	50	42.5	1.13	19	21.5	1.12	68

3	100	51.6	1.20	21	26.1	1.17	36
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^a Polymerization conditions: using **Ru-III** as catalyst, THF as solvent, $[M]_0 = 0.1$ mol/L, $T = 30$ °C, $t = 2$ h. ^bThe molar ratio of monomer to catalyst. ^cThe absolute molecular weight and polydispersity index calculated with light scattering data. ^dThe degree of polymerization calculated with absolute molecular weight. ^eThe relative molecular weight and polydispersity index calibrated with polystyrene standard. ^fThe isolated polymer yield.

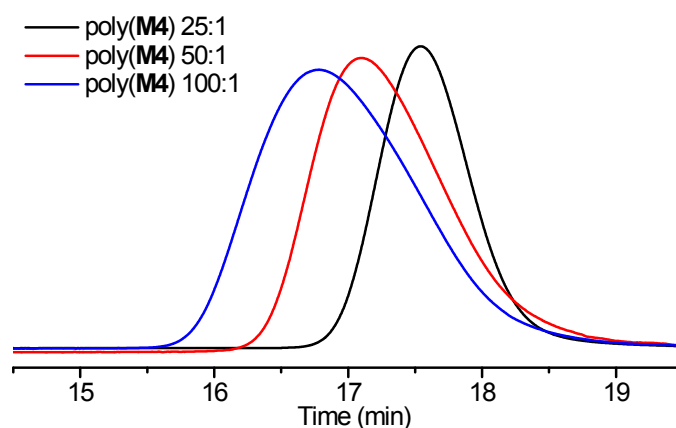


Fig. S5 Representative GPC traces of poly(**M4**) with different absolute molecular weights.

Self-Assembly Behavior of Triazole-Dendronized Polyacetylene

Depending on the backbone stiffness, the branch size, and the degree of coverage, the overall shape of dendronized polymers would be ball-like or wormlike.^{S6} The morphology of similar dendronized polymers were also reported as wormlike.^{S4,S7} Based on these reasons, we first prepared the sample of poly(**M1**) at 0.05 mg/mL in CHCl_3 , and regretfully the result failed to show wormlike morphology (Fig. S6a). The accumulation morphology might be resulted from high concentration of polymer solution, and that poly(**M1**) had a relative flexible backbone and a small branch size. Then, we prepared a poly(**M4**) sample at 0.005 mg/mL in CHCl_3 , while it was still observed that polymer aggregated together although poly(**M4**) had enough large branch size (Fig. S6b). Considering these phenomena, we supposed that the mutual repulsion action between the mica plate and 1,2,3-triazole groups forced polymers to aggregate together, on account of the mica plate containing negative charge and 1,2,3-triazole groups containing electron-rich nitrogen atoms.

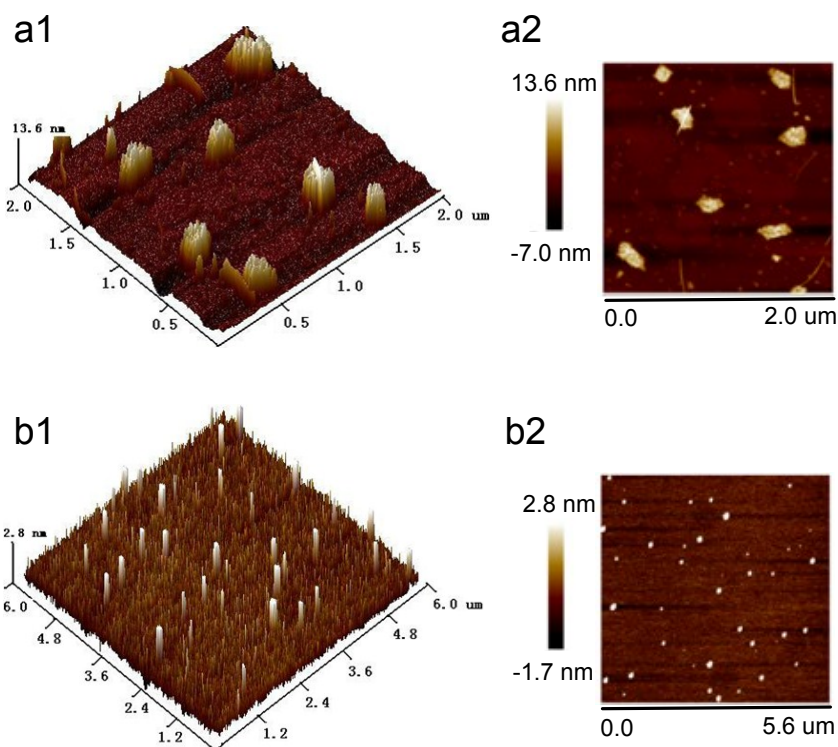


Fig. S6 AFM images of polymers in chloroform: (a) poly(**M1**) at 0.05 mg/mL, and (b) poly(**M4**) at 0.005 mg/mL. The left column reveals 3D images and the right column reveals 2D images.

REFERENCES

- (S1) J. M. Carney, P. J. Donoghue, W. M. Wuest, O. Wiest, and P. Helquist. *Org. Lett.*, 2008, **10**, 3903-3906.
- (S2) V. V. Rostovtsev, L. G. Green, V. V. Fokin, and K. B. Sharpless. *Angew. Chem. Int. Ed.*, 2002, **41**, 2596-2599.
- (S3) H. Ihre, A. Hult, J. M. J. Fréchet, and I. Gitsov. *Macromolecules*, 1998, **31**, 4061-4068.
- (S4) E-H Kang, I. S. Lee, and T-L Choi. *J. Am. Chem. Soc.*, 2011, **133**, 11904-11907.
- (S5) A. Zhang, B. Zhang, E. Wächtersbach, M. Schmidt, and A. D. Schlüter. *Chem. Eur. J.*, 2003, **9**, 6083-6092.
- (S6) N. Ouali, S. Méry, and A. Skoulios. *Macromolecules*, 2000, **33**, 6185-6193.
- (S7) H. Park, H-K Lee, E-H Kang, and T-L Choi. *J. Pol. Sci. Part A: Polym. Chem.*, 2015, **53**, 274-279.