Supporting Information

Living Light-Induced Crystallization-Driven Self-Assembly for Rapid Preparation of Semiconducting Nanofibers

Suyong Shin[1], Florian Menk[2], Youngjin Kim[3], Jeewoo Lim[3,4], Kookheon Char[3], Rudolf Zentel[2], and Tae-Lim Choi[1]*

[1]Department of Chemistry, Seoul National University, Seoul, 08826, Korea

[2]Institute for Organic Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128, Mainz, Germany

[3]Department of Chemical Engineering, Seoul National University, Seoul, 08826, Korea

[4]Department of Chemistry, Kyung Hee University, 26 Kyungheedae-ro, Dongdaemun-gu, Seoul, 02447, Korea

tlc@snu.ac.kr

Table of Contents

1. Experimental Details

1.1 General Experimental Considerations

Without additional notes, all reagents were commercially available from Acros, Alfa, Sigma Aldrich and TCI and used without further purification. 1,2-Dichloroethane was distilled under a nitrogen atmosphere over calcium hydride. Most of the reactions were monitored by thin-layer chromatography carried out on silica gel plates. Preparative separations were performed by column chromatography on silica gel grade 60 (0.040 – 0.063 mm) from Merck. All polymerizations were carried out under dry argon atmospheres using standard Schlenk-line techniques. THF was distilled over sodium and benzophenone and anhydrous deuterium THF solvent (≥ 99.95 %) were purchased from Euriso-Top®. THF solvents were degassed by argon bubbling for 10 minutes before polymerization. The third generation Grubbs catalyst was prepared by the reported method.[50] NMR spectra were recorded by Varian/Oxford As-500 (500 MHz for ^{1}H/125 MHz for ^{13}C) and Bruker Ascend TM-400 (400 MHz for ^{1}H/100 MHz for ^{13}C). THF size exclusion chromatography (SEC) for polymer molecular weight analysis was carried out with Waters system (1515 pump, 2424 refractive index detector) and Shodex GPC LF-804 column eluted with THF (GPC grade, Honeywell Burdick & Jackson). The flow rate was 1.0 mL/min and temperature of the column was maintained at 35 °C. THF solution of polymers (0.1 mg/mL) was injected into GPC after filtration using a 0.20 μm PTFE filter. UV/Vis spectra were obtained by Jasco Inc. UV/vis-Spectrometer V-630 and fluorescence spectra were obtained by FP-8300 (Jasco Inc.). Dynamic Light Scattering (DLS) data were obtained by Malvern Zetasizer Nano ZS. Film state X-ray diffraction (XRD) was performed by the National Instrumentation Center for Environmental Management (NICEM) at SNU using D8 Discover with GADDS (Bruker, Germany). Differential scanning calorimetry (DSC) was carried out under N_2 gas at a scan rate of 5 ℃/min with Q10 model devices from TA Instruments. IR spectra were measured on a Thermo Scientific Nicolet 6700 spectrometer. Cyclic voltammetry (CV) measurements were carried out

on a CHI 660 Electrochemical Analyzer (CH Instruments, Insc., Texas, USA) using a degassed acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M).

1-2. *In Situ* ^{1}H NMR Analysis

157 μmol of **1a,** 62.8 μmol of **2** and hexamethyldisilane (~3 mg, an internal standard) were added into NMR tube and purged with argon. Anhydrous and degassed deuterated THF was added (550 μL) to the NMR tube and stabilized at 0 °C in NMR instrument. Then, the initial ratio of all compounds was measured by ^{1}H NMR analysis. After that, the solution of the third-generation Grubbs catalyst (3.14 μmol, 70 μL, 0 °C) was added and the conversion of the two monomers was monitored by every 1 minutes. The measurement was done by Avance-500 (500 MHz for ^{1}H, Bruker, Germany) in the National center for Inter-University Research Facilities (NCIRF) at SNU.

1-3. LI-CDSA and Seeded Growth of Nanofibers

P1a$_{20}$-*b*-**P2**$_{15}$ or **P1b**$_{50}$-*b*-**P2**$_{15}$ was dissolved in THF (0.1 mg/mL) and kept the solution under the light using fluorescent light (for 2 hours) or 5W white LED (for 5 minutes) as the light source at different temperatures. For seeded growth, seed micelles were prepared by sonicating the original long nanofibers (0.1 mg/mL) at 0 °C for 30 min. Different aliquots (1, 1.5, 2, 2, and 1.5 mL) of THF solution of unimers (0.1 mg/mL) were added into a seed solution (0.1 mg/ml, 0.5, 0.3, 0.2, 0.1, and 0.03 ml, respectively). The samples were kept under the light using fluorescent light (for 2 hours) or 5W white LED (for 5 minutes) as the light source at different temperatures.

1-4. Light On-and-Off Experiment

P1b$_{50}$-*b*-**P2**$_{15}$ was dissolved in THF (0.1 mg/mL) and kept the solution under the light using 5W white LED (for 5 minutes) as the light source at room temperature. Then, the solution was sonicated at 0 °C for 30 min to prepare seed micelles. 0.1 mL of seed solution was added to 5 mL

of **P1b**$_{50}$-*b*-**P2**$_{15}$ unimer solution (0.1 mg/mL in THF, unimer-to-seed ratio 50) and the mixture solution was kept under 5W white LED for short time (30 sec) at room temperature and analyzed immediately by UV/vis and DLS, and also immediately prepared sample for TEM imaging by taking aliquot of the solution. During the analyses, the remaining sample was stored at dark room and the same analyses were done after 30 min. This light on-off cycle was repeated using different "on" time, 30, 30, 60 and 120 seconds for each cycle.

1-5. Preparation of ABA Block Comicelles

P1a$_{20}$-*b*-**P2**$_{15}$ was dissolved in THF (0.1 mg/mL) and kept the solution under the light using 5W white LED (for 5 minutes) as the light source at room temperature. Then, the solution was sonicated at 0 ^{o}C for 30 min to prepare initial seed micelles. 0.1 mL of initial seed solution was added to 0.2 mL of **P1a**$_{20}$-*b*-**P2**$_{15}$ unimer solution (0.1 mg/mL in THF, unimer-to-seed ratio 2) and the mixture solution was kept under 5W white LED for 5 min at room temperature. 0.2 mL of the resulting **P1a**$_{20}$-*b*-**P2**$_{15}$ seed solution for block comicelles was added to 2.8 mL of **P1b**$_{50}$-*b*-**P2**$_{15}$ unimer solution (0.1 mg/mL in THF, unimer-to-seed ratio 4) followed by LED irradiation for 5 min for seeded growth to produce block comicellles.

1-6. Preparation of Gradient Comicelles

P1a$_{20}$-*b*-**P2**$_{15}$ was dissolved in THF (0.1 mg/mL) and kept the solution under the light using 5W white LED (for 5 minutes) as the light source at room temperature. Then, the solution was sonicated at 0 ^{o}C for 30 min to prepare initial seed micelles. 0.05 mL of initial seed solution was added to 0.5 mL of **P1a**$_{20}$-*b*-**P2**$_{15}$ unimer solution (0.1 mg/mL in THF, unimer-to-seed ratio 10) and the mixture solution was kept under 5W white LED for 15 sec at room temperature. 1.7 mL of **P1b**$_{50}$-*b*-**P2**$_{15}$ unimer solution (0.1 mg/mL in THF, unimer-to-seed ratio 10) was added to the partially isomerized **P1a**$_{20}$-*b*-**P2**$_{15}$ solution followed by LED irradiation for 5 min to produce gradient comicellles.

1-7. Preparation of Random Comicelles

P1a$_{20}$-*b*-**P2**$_{15}$ was dissolved in THF (0.1 mg/mL) and kept the solution under the light using 5W white LED (for 5 minutes) as the light source at room temperature. Then, the solution was sonicated at 0 ºC for 30 min to prepare initial seed micelles. To 0.05 mL of initial seed solution, 0.5 mL of **P1a**$_{20}$-*b*-**P2**$_{15}$ unimer solution (0.1 mg/mL in THF, unimer-to-seed ratio 10) and 1.7 mL of **P1b**$_{50}$-*b*-**P2**$_{15}$ unimer solution (0.1 mg/mL in THF, unimer-to-seed ratio 10) were added. LED irradiation for 5 min produced random comicellles.

1-8. Atomic Force Microscopy

Multimode 8 and Nanoscope V controller (Veeco Instrument) were used for AFM imaging. All images were obtained on tapping mode using noncontact mode tip from Nanoworld (Pointprobe tip, NCHR type) with spring constant of 42 N m^{-1} and tip radius of $\leq$ 8 nm. The samples were prepared by spin-coating one drop of the polymer solution (~0.03 mg/mL THF, 3000 rpm for 30 sec) on a glass substrate.

1-9. Transmission Electron Microscopy

TEM imaging was performed by JEM-2100 operated at 120 kV and equipped with SC 1000 CCD camera (Gatan Inc.). The samples were prepared by spin-coating one drop of the polymer solution (~0.03 mg/mL THF, 3000 rpm for 10 sec) on the carbon-coated copper grid. For the samples stained by phosphotungstic acid, one drop of phosphotungstic acid aqueous solution (1.0 mg/ml) was added onto the dried grid surface with samples, and most of the solution on the grid was absorbed by filter paper after 1 minute and the grid was dried at room temperature. For each sample, length distributions of fiber-like micelles were calculated by measuring about 100 structures using Gatan Digital Micrograph software. Values of the number-average length (L_n), weight-average length (L_w), standard deviation (σ) and polydispersity index (PDI) of micelles were calculated as

follows where *N* is the sample size.

$$L_n = \frac{\sum_{i=1}^{n} N_i L_i}{\sum_{i=1}^{n} N_i}$$

$$L_w = \frac{\sum_{i=1}^{n} N_i L_i^2}{\sum_{i=1}^{n} N_i L_i}$$

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{n}(x_i - \mu)^2}$$

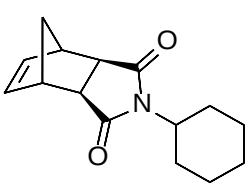
$$\text{PDI} = \frac{L_w}{L_n}$$

1-10. Cryo-Transmission Electron Microscopy

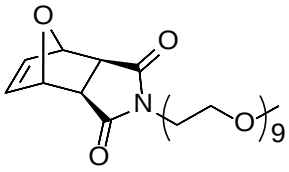
The cryo-TEM experiments were performed with a thin film of solution (5 μL, 0.1 mg/mL) transferred to a lacey supported grid. The thin solution films were prepared under solvent vapor saturated condition (THF) within a custom-built environmental chamber in order to prevent evaporation of solvent from sample solution. The excess liquid was blotted with filter paper for 3 seconds, and the thin solution films were rapidly vitrified by plunging them into liquid nitrogen (-200 °C) using Gatan CryoplungeTM3 system. The grid was transferred on a Gatan 626 cryoholder, using a cryo-transfer device. After that they were transferred to a JEM-2100. Direct imaging was carried out at a temperature of approximately -175 °C and with a 120 kV accelerating voltage.

2. Synthetic Information

2-1. Synthesis of Monomers



1a



1b

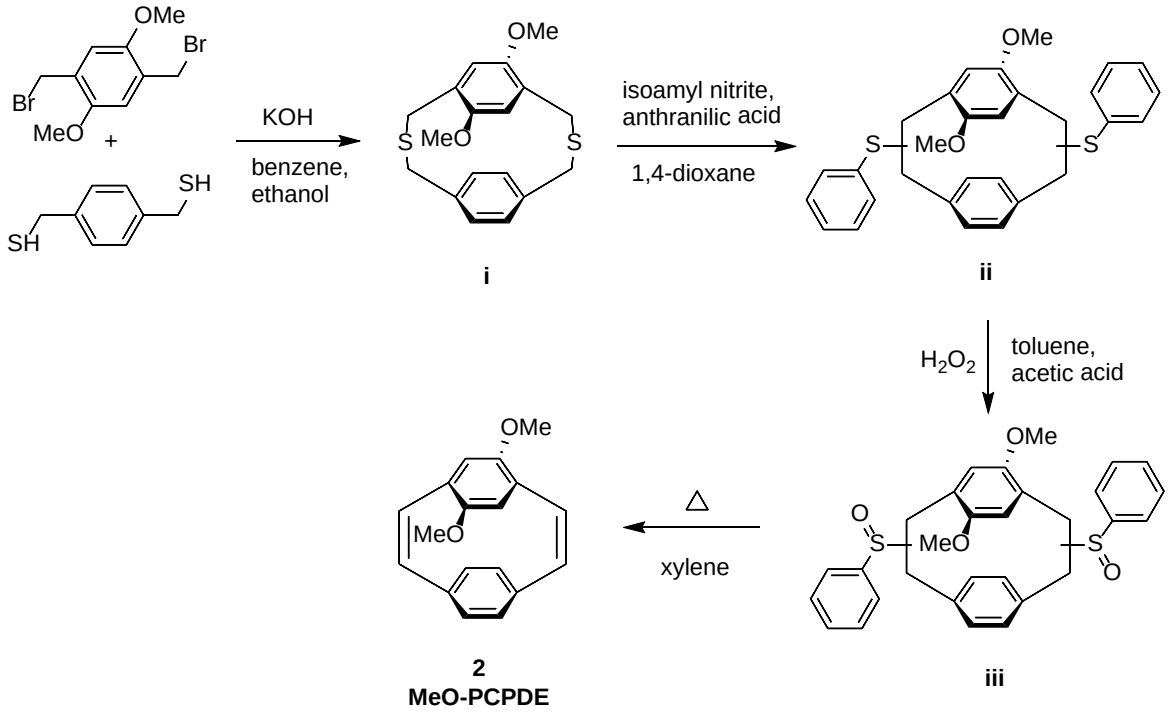
Both monomers were prepared by the method from the previous literatures.[1, 2]

_N_-cyclohexyl-_exo_-norbornene-5,6-dicarboximide (1a)

^{1}H NMR (500 MHz, $CDCl_3$) : δ 6.27 (s, 2H), 3.91-3.96 (m, 1H), 3.25 (s, 2H), 2.60 (s, 2H), 2.10-2.18 (m, 2H), 1.20-1.83 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) : δ 178.22, 137.88, 51.60, 47.43, 45.42, 42.58, 28.78, 25.85, 25.07

exo-_N_-PEG-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (1b)

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.51 (s, 2 H), 5.26 (s, 2 H), 3.59-3.70 (m, 34 H), 3.54-3.56 (m, 2 H), 3.38 (s, 3 H), 2.85 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.15, 136.60, 80.94, 71.99, 70.63, 70.13, 67.16, 59.09, 47.53, 38.22



Supplementary Scheme 1. Synthetic routes to 4,7-dimethoxy[2,2]paracyclooctaphane-1,9-diene.

Synthesis of 4,7-dimethoxy-2,11-dithia[3,3]-paracyclophane (i)

A deoxygenated mixture of 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (2.52 g, 14.7 mmol) and 1,4-bis(thiolatomethyl)benzene (4.80 g, 14.8 mmol) in benzene (660 mL) was added dropwise to a solution of KOH (3.98 g, 71.1 mmol) in ethanol (530 mL) under a nitrogen atmosphere for a period at least 72 hours. After a further 2 hours, the solvent was evaporated and the residue was extracted with HCl and DCM. The organic layers were combined, washed by water, dried with anhydrous $MgSO_4$, filtered and evaporated. The residue were purified by column chromatography with using DCM:hexane (2:1) as the eluent. The cyclic compound was obtained as white solids in a yield of 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90-6.98 (m, 4H), 6.46 (s, 2H), 4.23-4.26 (d, 2H), 3.74-3.85 (m, 10H), 3.35-3.39 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.39, 136.63, 129.12, 128.19, 124.98, 113.88, 55.65, 37.99, 31.17. HRMS (EI, $[M]^+$): calculated for $[C_{18}H_{21}O_2S_2]^+$: *m/z* 332.0905, found *m/z* 332.0906.

Synthesis of bis(sulfide) compounds (ii)

Isoamyl nitrite (5.84 mL, 43.5 mmol) was added dropwise into a solution of anthranilic acid (3.50 g, 25.5 mmol) and compound **i** (2.43 g, 7.3 mmol) in anhydrous 1,4-dioxane (190 mL) under reflux and a nitrogen atmosphere without light at least 15 minutes. The reaction mixture was boiled under reflux for another 3 hours. After the reaction mixture was concentrated under reduced pressure, the residue was purified by column chromatography using a solvent system of DCM and hexane (1:4). The cyclic compound was obtained as yellow solids in a yield of 43%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.46 (m, 4H), 7.14-7.18 (m, 4H), 7.08-7.14 (m, 2H), 6.40-6.85 (m, 4H), 5.75-6.31 (m, 2H), 4.84-5.38 (m, 2H), 3.66-3.79 (m, 8H), 2.36-2.79 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.55, 152.35, 139.55, 138.50, 136.89, 136.61, 133.72, 131.74, 131.53, 130.62, 129.94, 129.57, 129.14, 129.06, 128.91, 128.87, 128.79, 128.45, 127.87, 127.58, 126.55, 125.87, 119.63, 115.65, 55.92, 55.57, 54.89, 51.05, 44.24, 43.83, 43.51, 43.22, 40.67. HRMS (EI, $[M]^+$): calculated for $[C_{30}H_{29}O_2S_2]^+$: *m/z* 484.1531, found *m/z* 484.1528.

Synthesis of bis(sulfoxide) compounds (iii)

Hydrogen peroxide (0.75 mL, 34.5wt%) was added dropwise to the solution of compound **ii** (1.66 g, 3.43 mmol) in toluene (88 mL) and acetic acid (28 mL) at 0^{o}C under a nitrogen atmosphere over a period of 20 minutes. The mixture was allowed to warm up to room temperature and stirred for additional 18 hours. The resulting solution was then extracted successively with brine and DCM, dried with $MgSO_4$ and concentrated to give pale yellow oil in an overall yield of 99%. The compounds contain a large number of stereoisomers and were used as starting materials for the next step without purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.79 (m, 4H), 7.51-7.60 (m, 4H), 7.18-7.21 (m, 2H), 6.44-6.77 (m, 4H), 5.32-6.14 (m, 2H), 4.65-4.78 (m, 2H), 3.53-3.74 (m, 8H), 2.78-2.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.29, 152.99, 152.71, 137.43, 134.92, 134.36, 132.42, 131.98, 130.92, 129.75, 129.23, 128.33, 125.48, 124.55, 123.79, 121.36, 120.27, 119.31, 117.77, 68.09, 60.84, 56.21, 55.56, 54.76, 32.07, 31.01, 29.82. HRMS (EI, $[MH]^+$):

calculated for $[C_{30}H_{29}O_4S_2]^+$: *m/z* 516.1429, found *m/z* 517.1509.

Synthesis of 4,7-dimethoxy[2,2]paracyclooctaphane-1,9-diene (2, MeO-PCPDE)

A solution of compound **iii** in xylene was refluxed under a nitrogen stream for 20 hours. The solution was cooled to room temperature and extracted successively with dilute aqueous HCl and DCM, dried with anhydrous $MgSO_4$, filtered and concentrate. The crude compound was then chromatographed over silica gel using DCM:hexane (1:6) for elution and gave compound **2** (MeO-PCPDE) as white solids in a yield of 25%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.16 (d, 2H), 6.92-6.94 (d, 2H), 6.81-6.83 (m, 2H), 6.47-6.50 (m, 2H), 5.80 (s, 2H), 3.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.42, 137.82, 135.60, 133.84, 130.93, 127.05, 126.58, 118.76, 55.61. HRMS (EI, $[M]^+$): calculated for $[C_{18}H_{17}O_2]^+$: *m/z* 264.1150, found *m/z* 264.1154.

2-2. Synthesis of Polymers

General procedure for the one-shot ROMP

Both comonomers (25.2-62.8 μmol for **1a** or **1b** and 18.9-25.2 μmol for **2**) were weighed into a 2 mL sized screw-cap vial with a septum and purged with argon. Anhydrous and degassed THF was added (160-230 μL) to the vial. THF solution of the third-generation Grubbs catalyst (1.26 μmol) was added (20 μL) to the monomer solution at once under vigorous stirring. The mixture was stirred for 5 min at rt and then 7 h at 40 °C. The reaction was quenched by excess ethyl vinyl ether. The crude mixture was precipitated into methanol (**P1a**-*b*-**P2**) or cold ether at -78 °C (**P1b**-*b*-**P2**), and the obtained powder or sticky gel was dried in vacuo.

General procedure to prepare homopolymers ($P1a_{50}$, $P1b_{50}$ and $P2_{15}$) by ROMP.

1a, **1b** (62.8 μmol) or **2** (18.9 μmol) were weighed in a 2-mL sized screw-cap vial with septum and purged with argon. Anhydrous and degassed THF was added (160 μL) to the vial. The THF

solution of the third-generation Grubbs catalyst (1.26 μmol) was added (20 μL) to the monomer solution at once under vigorous stirring. After 10 minutes for **P1a**$_{50}$ and **P1b**$_{50}$ at room temperature and after 7 for **P2**$_{15}$ at 40 °C, the reaction was quenched by excess ethyl vinyl ether. The crude mixture was precipitated into methanol (**P1a**$_{50}$ and **P2**$_{15}$) or cold ether at -78 °C (**P1b**$_{50}$), and the obtained powder or sticky gel was dried *in vacuo*.

Preparation of P1a$_{50}$-*b*-P2$_{20}$ by ROMP via conventional sequential monomer addition.

1a (62.8 μmol) were weighed in a 2-mL sized screw-cap vial with septum and purged with argon. Anhydrous and degassed THF was added (160 μL) to the vial. The THF solution of the third-generation Grubbs catalyst (1.26 μmol) was added (20 μL) to the monomer solution at once under vigorous stirring. After 10 minutes, the THF solution of PCPDE (25.2 μmol) was added (80 μL), and the mixture was stirred for 7 h at 40 °C. The reaction was quenched by excess ethyl vinyl ether. The crude mixture was precipitated into methanol and the obtained powder was dried *in vacuo*.

P1a-*b*-P2 one-shot copolymers

Yield: 90-98% (see Table 1, entry 1 and 5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01-7.42 (m), 6.61-6.82 (m) 5.76 (m), 5.47-5.52 (m), 3.87 (s), 3.44-3.51 (m), 3.27 (s), 2.67-3.04 (m), 2.12 (m), 1.81 (s), 1.58-1.64 (m), 1.21-1.29 (m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.5, 151.8, 150.9, 134.0, 132.2, 131.9, 130.1, 129.5, 126.4, 113.3, 109.0, 56.1, 52.5, 51.6, 50.8, 46.2, 42.4, 41.0, 29.0, 26.1, 25.3. (all **P1a**-*b*-**P2** one-shot copolymers have identical ^{1}H-NMR and ^{13}C-NMR spectra except for integration of each block)

P1b-*b*-P2 one-shot copolymer

Yield: 95% (see Table 1, entry 4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99-7.40 (m), 6.57-6.80 (m), 6.08 (s), 5.75-5.78 (d), 4.94-5.01 (m), 4.44 (s), 3.85 (s), 3.42-3.65 (m), 3.37 (s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.6, 151.9, 150.9, 132.0, 131.1, 129.5, 127.6, 126.3, 113.6, 109.1, 81.1, 72.1,

70.7, 70.1, 67.0, 59.2, 56.0, 53.6, 52.7, 38.3, 29.8.

P1a-*b*-P2 conventional copolymer

Yield: 98% (see Table 1 entry 3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01-7.42 (m), 6.61-6.82 (m) 5.76 (m), 5.47-5.52 (m), 3.87 (s), 3.44-3.51 (m), 3.27 (s), 2.67-3.04 (m), 2.12 (m), 1.81 (s), 1.58-1.64 (m), 1.21-1.29 (m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.5, 151.8, 150.9, 134.0, 132.2, 131.9, 130.1, 129.5, 126.4, 113.3, 109.0, 56.1, 52.5, 51.6, 50.8, 46.2, 42.4, 41.0, 29.0, 26.1, 25.3.

P1a homopolymer

Yield: 97% (see Table 1 entry 2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.72-5.74 (m), 5.45-5.50 (m), 3.85 (s), 3.25 (s), 2.65-3.01 (m), 2.10 (m), 1.79 (s), 1.54-1.61 (m), 1.20-1.27 (m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.6, 133.8, 132.0, 52.9, 52.6, 51.5, 50.9, 46.1, 42.4, 41.0, 28.9, 26.0, 25.2.

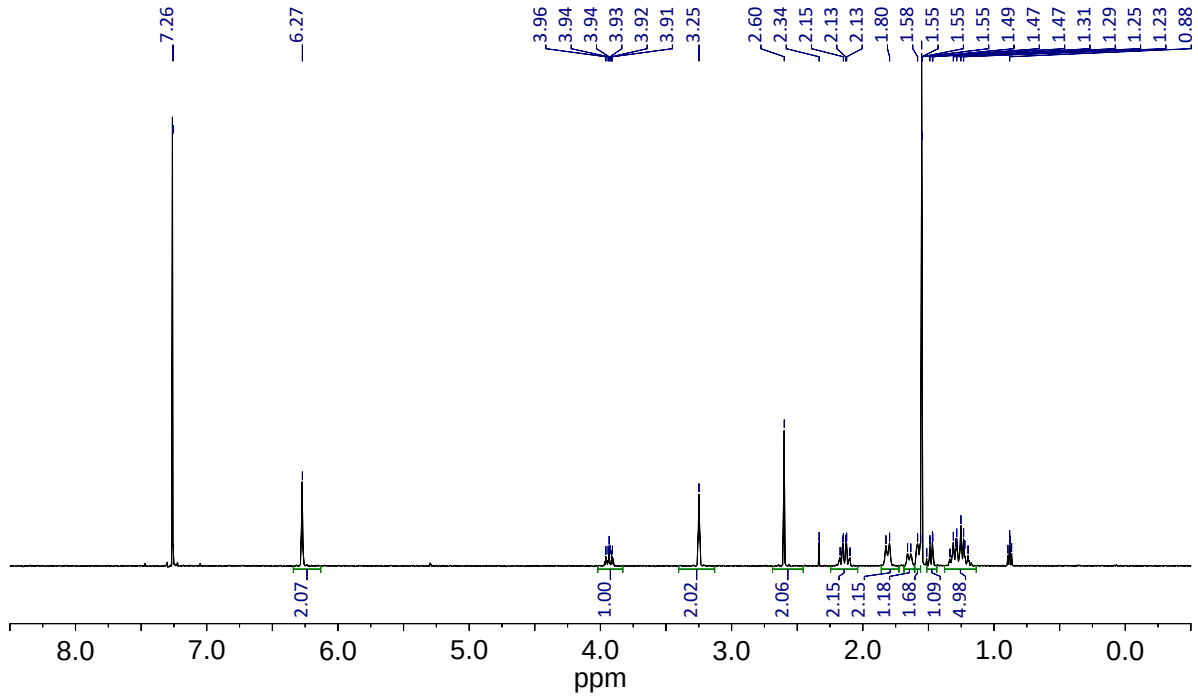
P1b homopolymer

Yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.06 (s), 5.77 (m), 4.93-5.00 (m), 4.43 (s), 3.53-3.62 (m), 3.36 (s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.6, 131.8, 131.1, 81.0, 72.0, 70.6, 70.0, 66.9, 59.1, 53.5, 52.5, 38.1.

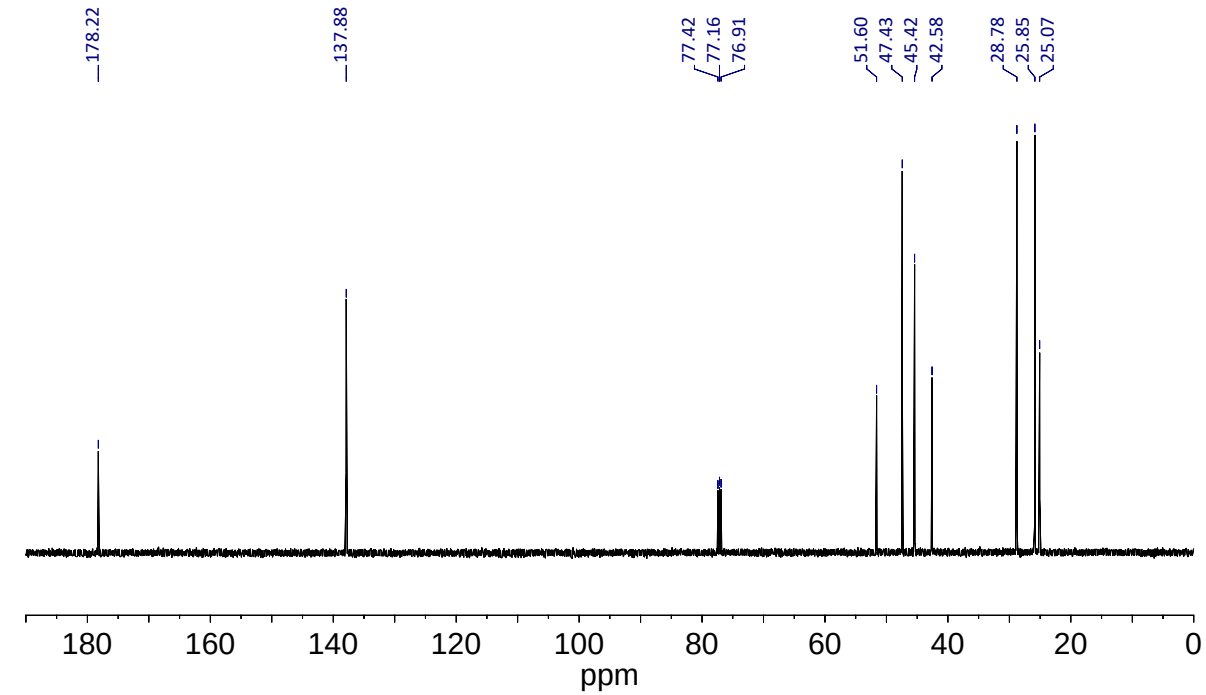
P2 homopolymer

Yield: 91%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00-7.42 (m), 6.61-6.81 (m), 3.86 (s), 3.43-3.50 (m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 150.8, 136.9, 136.7, 136.2, 130.1, 129.5, 128.8, 128.2, 127.0, 126.4, 126.3, 125.5, 123.5, 123.1, 113.3, 112.9, 108.9, 108.8, 56.3, 56.1, 56.0, 25.8, 21.3.

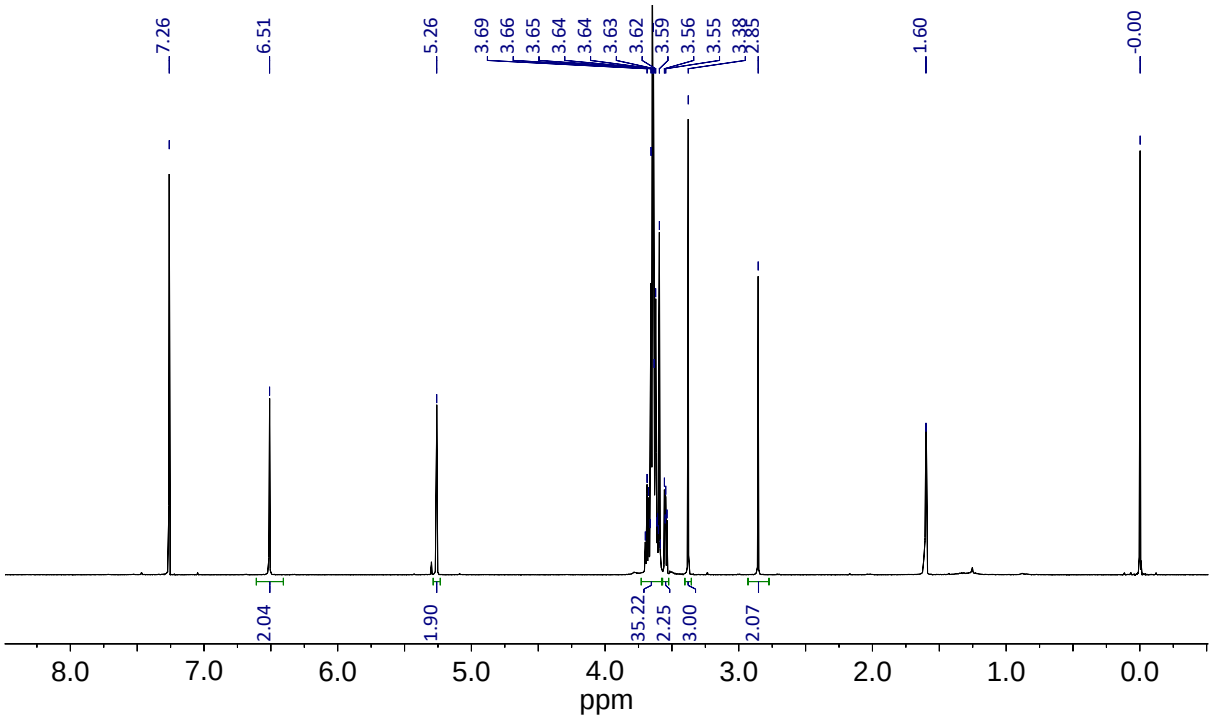
2-3. ^{1}H and ^{13}C NMR Spectra of the Substrates and the Polymers



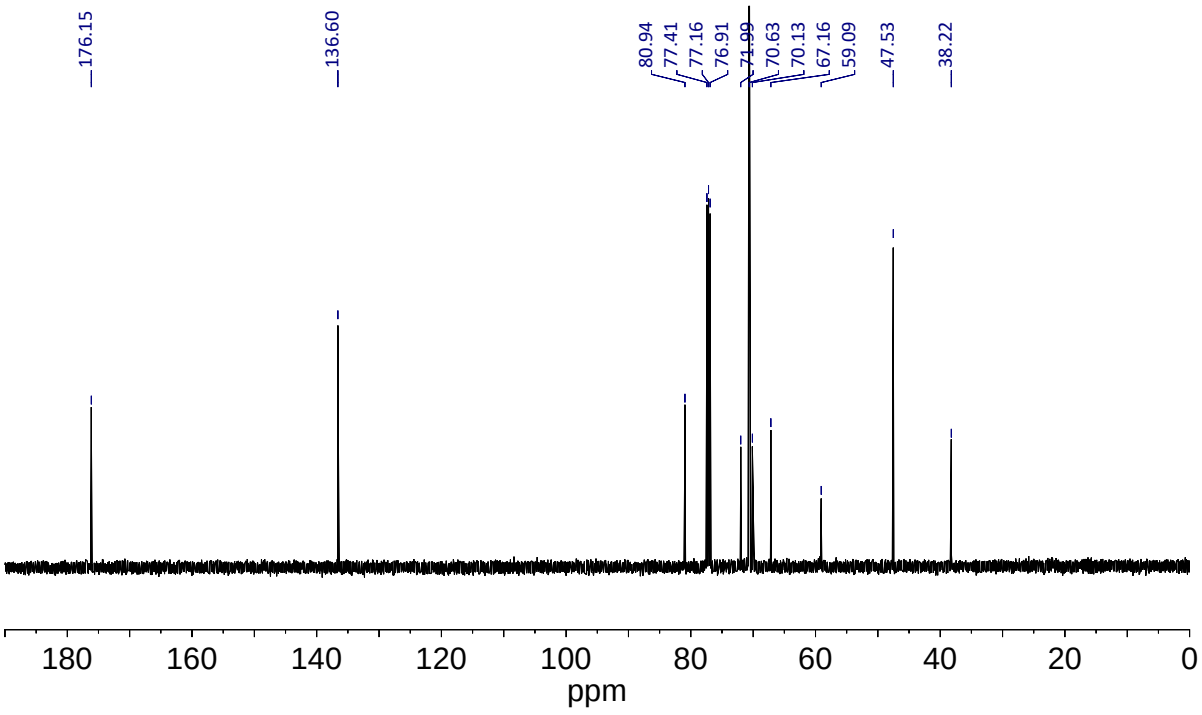
The ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *N*-cyclohexyl-*exo*-norbornene-5,6-dicarboximide (**1a**)



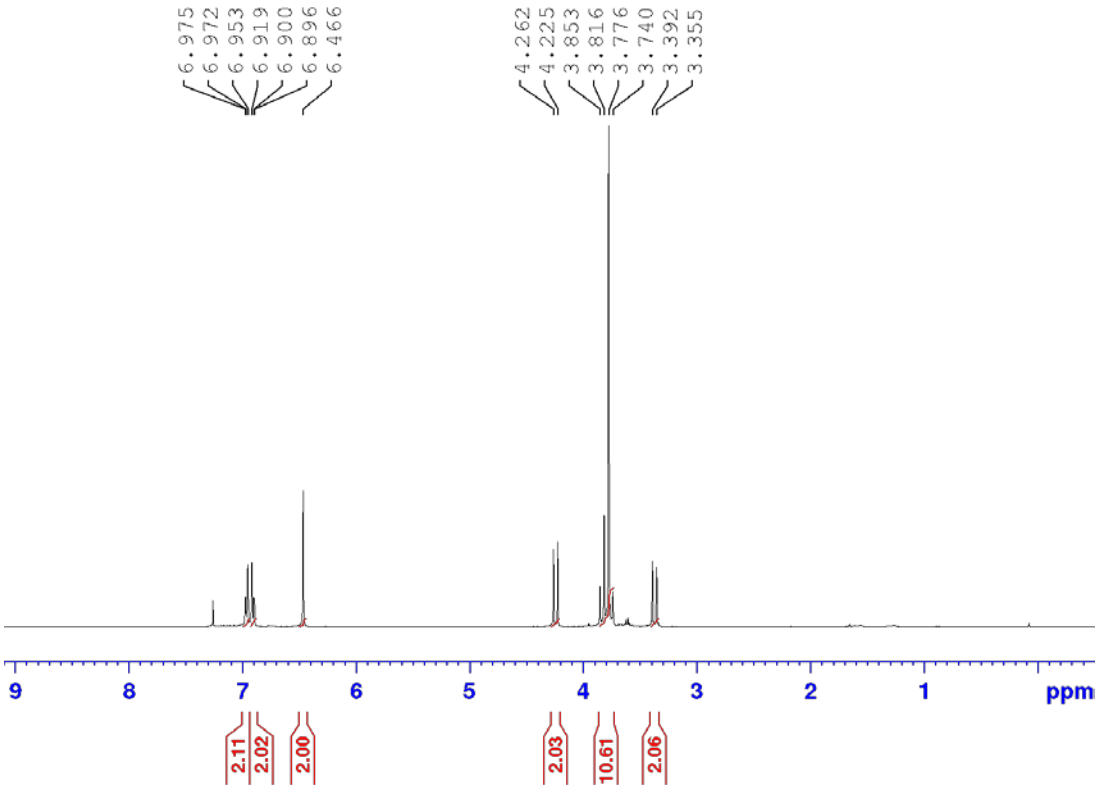
The ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *N*-cyclohexyl-*exo*-norbornene-5,6-dicarboximide (**1a**)



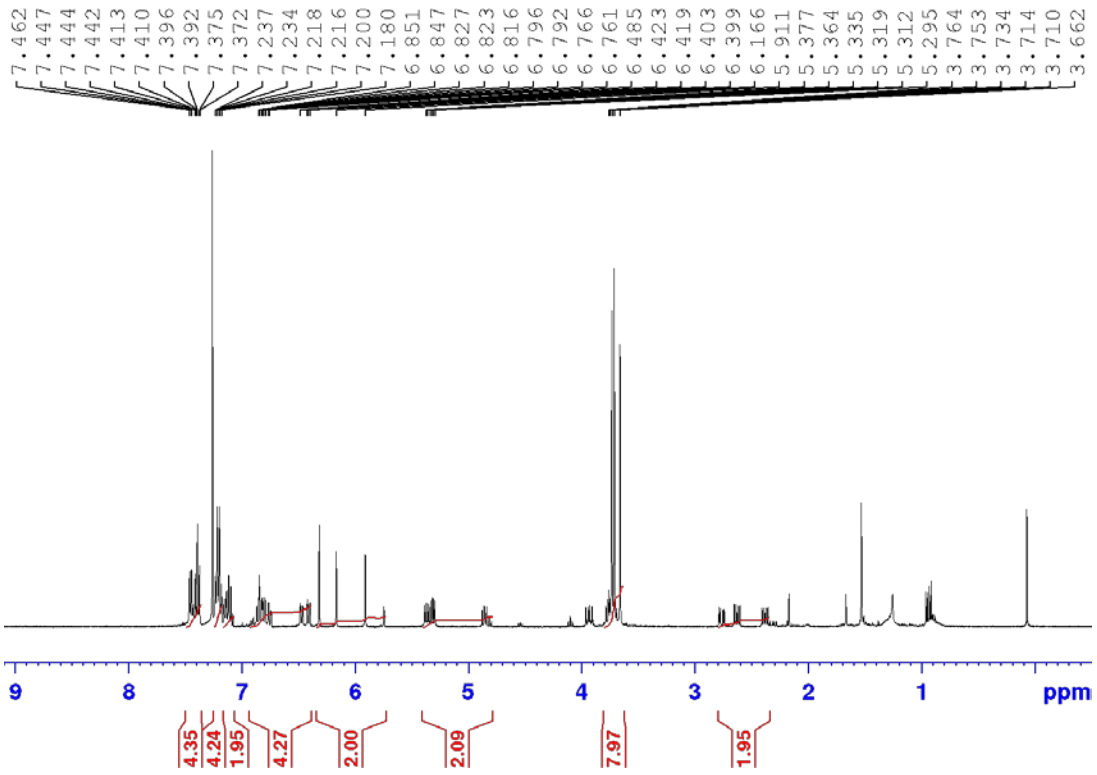
The ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of exo-*N*-PEG-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**1b**)



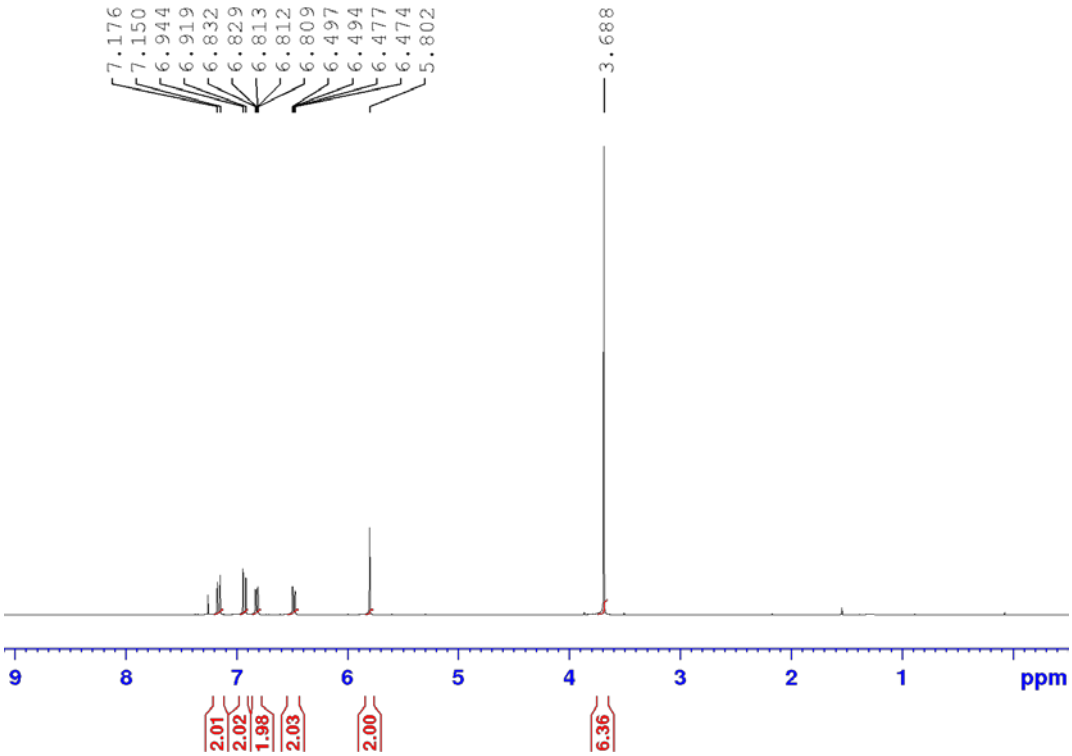
The ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of exo-*N*-PEG-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**1b**)



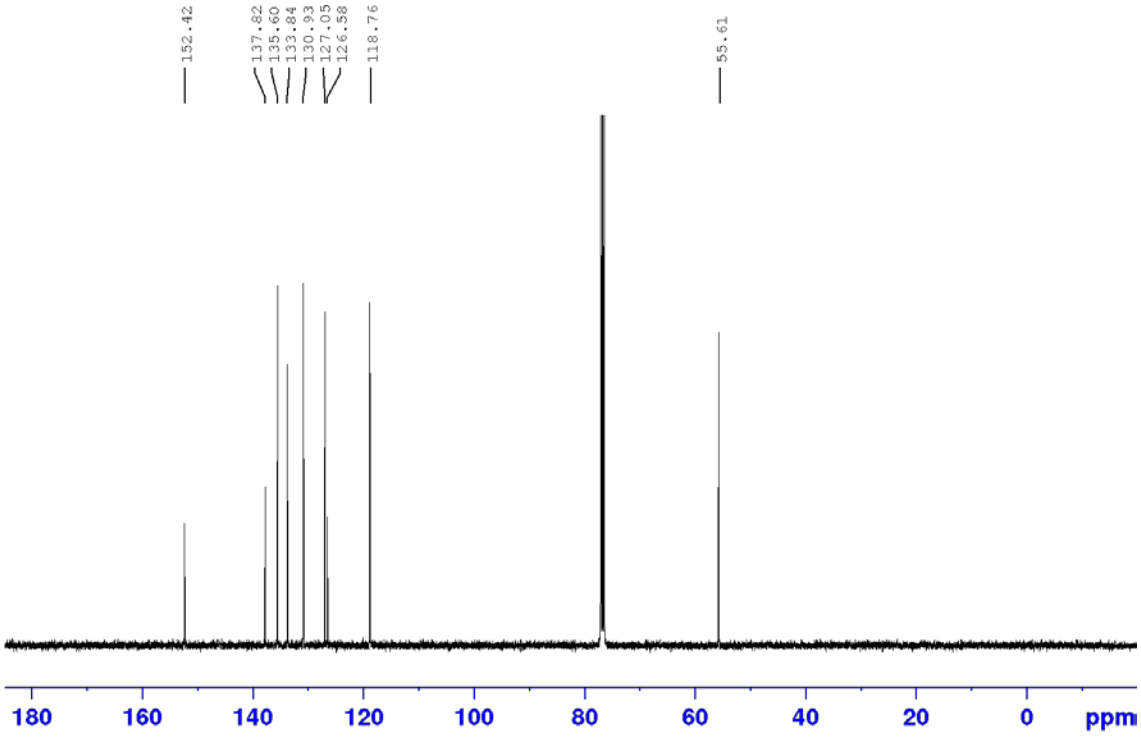
The ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,7-dimethoxy-2,11-dithia[3,3]-paracyclophane **(i)**.



The ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of bis(sulfide) compounds **(ii)**.

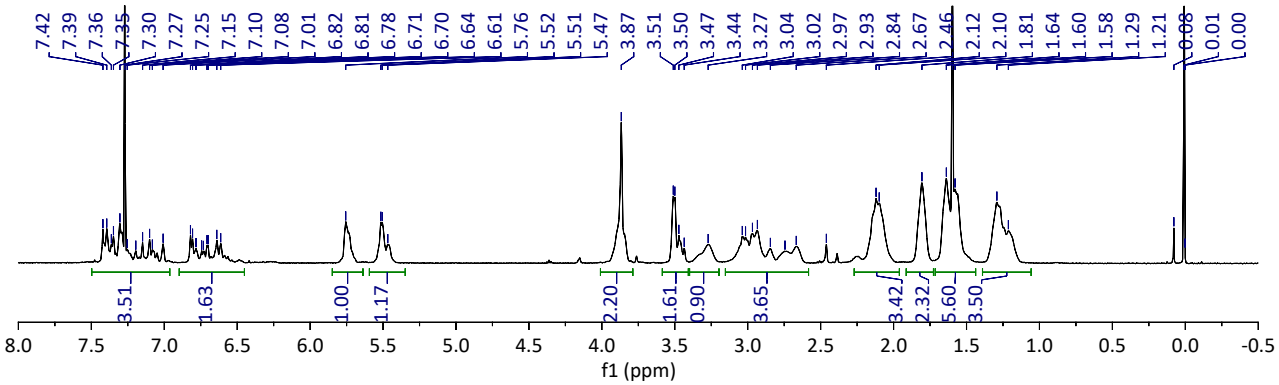


The ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,7-dimethoxy[2,2]paracyclooctaphane-1,9-diene **(2**, MeO-PCPDE**)**.

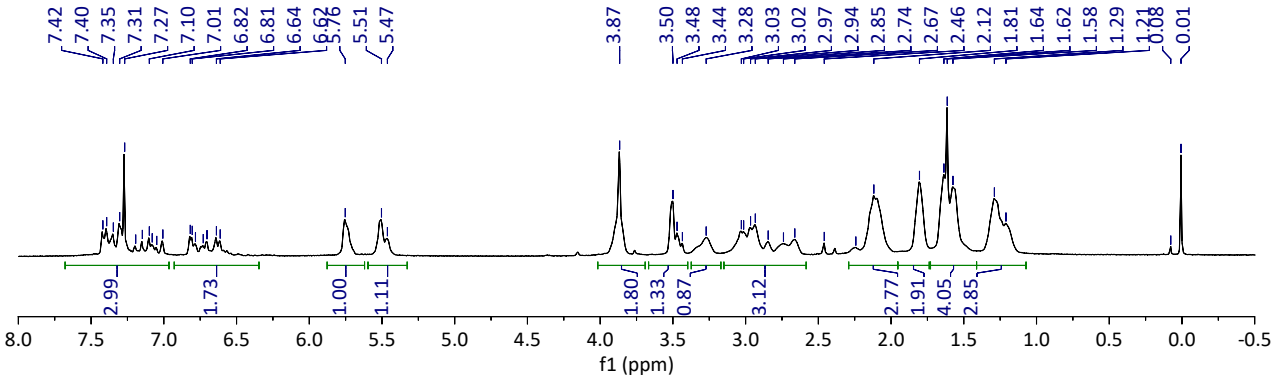


The ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4,7-dimethoxy[2,2]paracyclooctaphane-1,9-diene **(2**, MeO-PCPDE**)**.

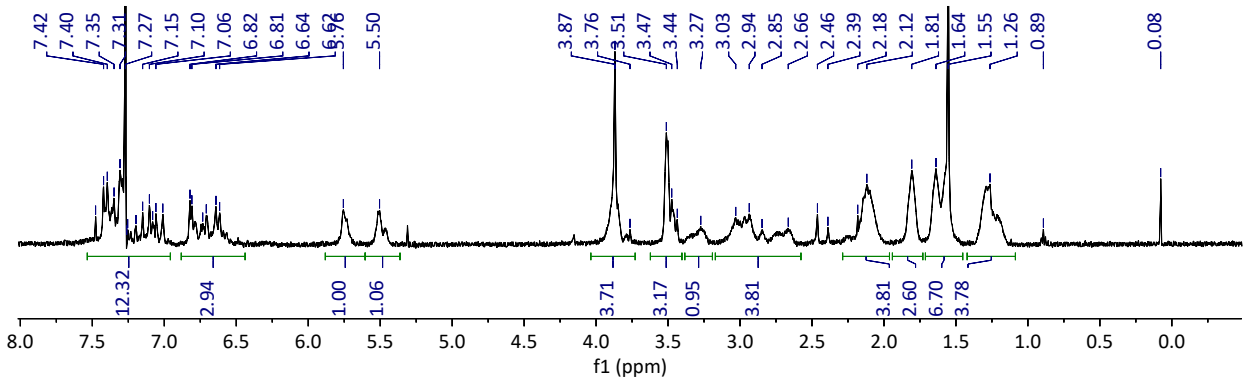
P1a$_{50}$-*b*-P2$_{20}$ one-shot copolymer



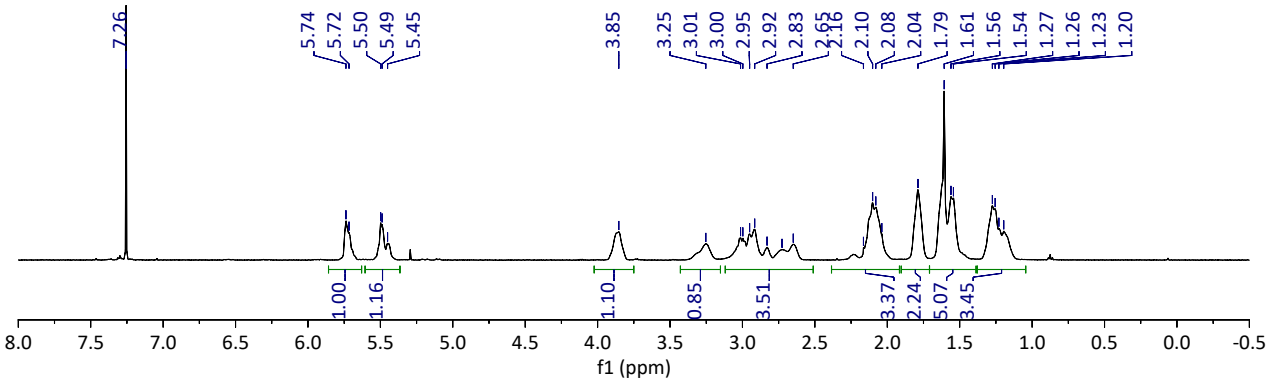
P1a$_{50}$-*b*-P2$_{20}$ conventional copolymer



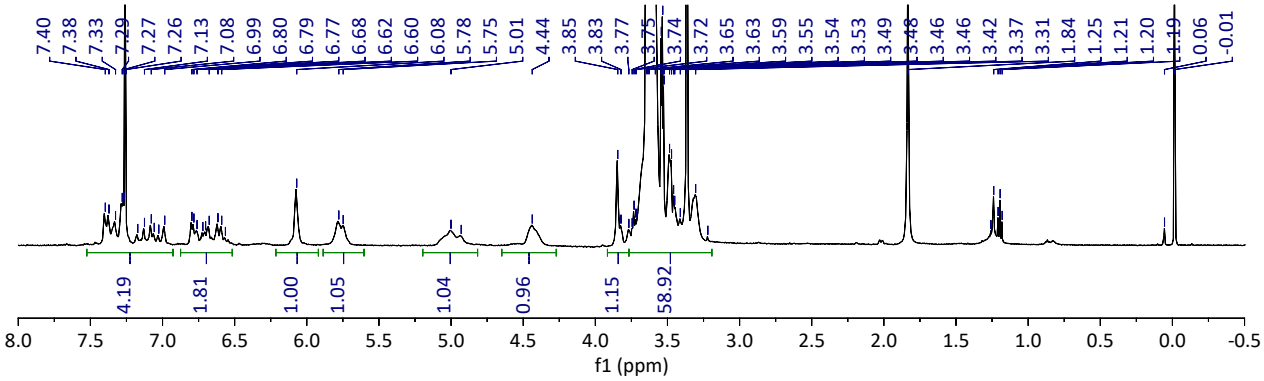
P1a$_{20}$-*b*-P2$_{15}$ one-shot copolymer



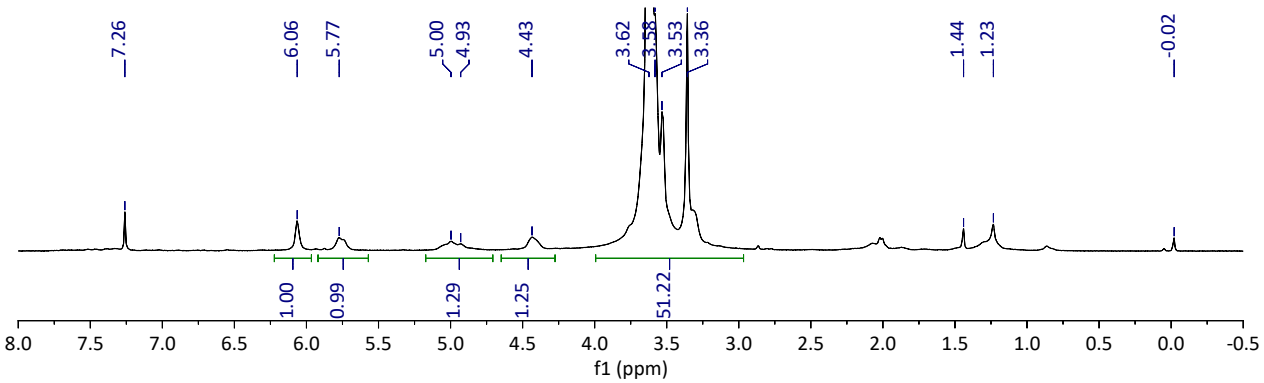
P1a$_{50}$ homopolymer



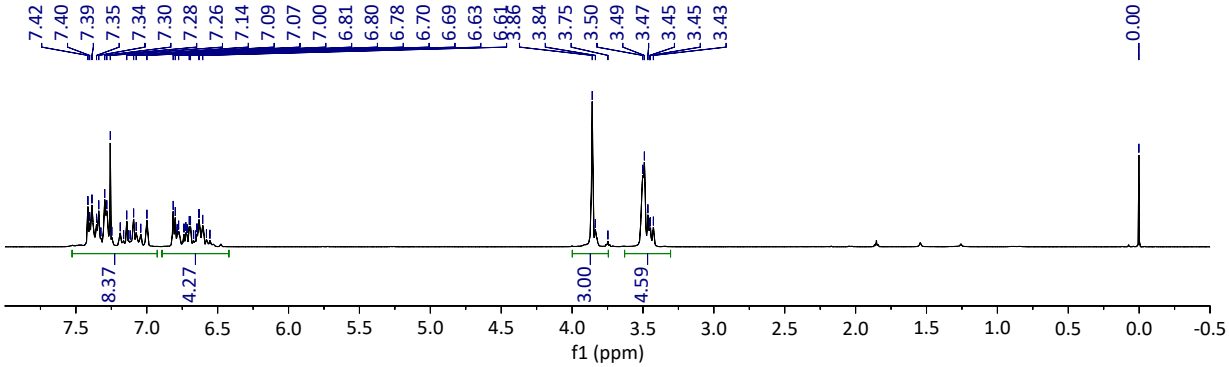
P1b$_{20}$-*b*-P2$_{15}$ one-shot copolymer



P1b$_{50}$ homopolymer



P2$_{15}$ homopolymer



3. Supporting Tables and Figures

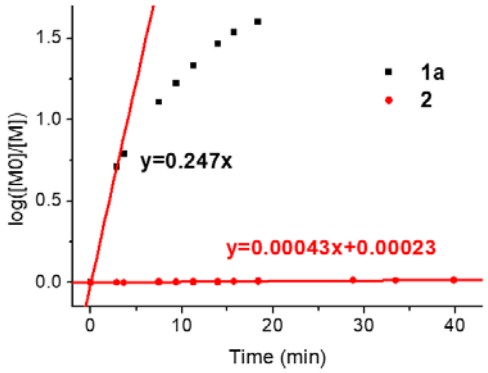


Figure S1. Logarithmic conversion vs time plot for one-shot ROMP of **1a** and **2** with feed ratio [**1b**]:[**2**]=50:20 at 0.1 M based on the concentration of **2** in THF.

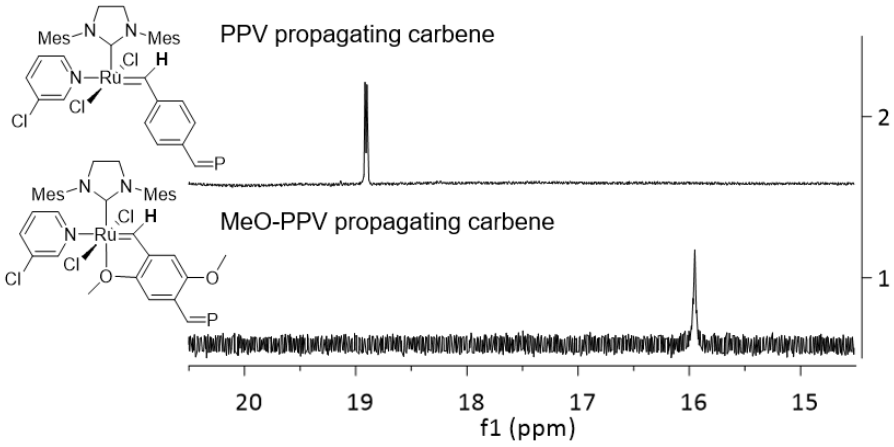


Figure S2. ^{1}H NMR spectra of propagating carbene signals during polymerization of PPV (top)[3] and **P2** (MeO-PPV, down) in d_8-THF.

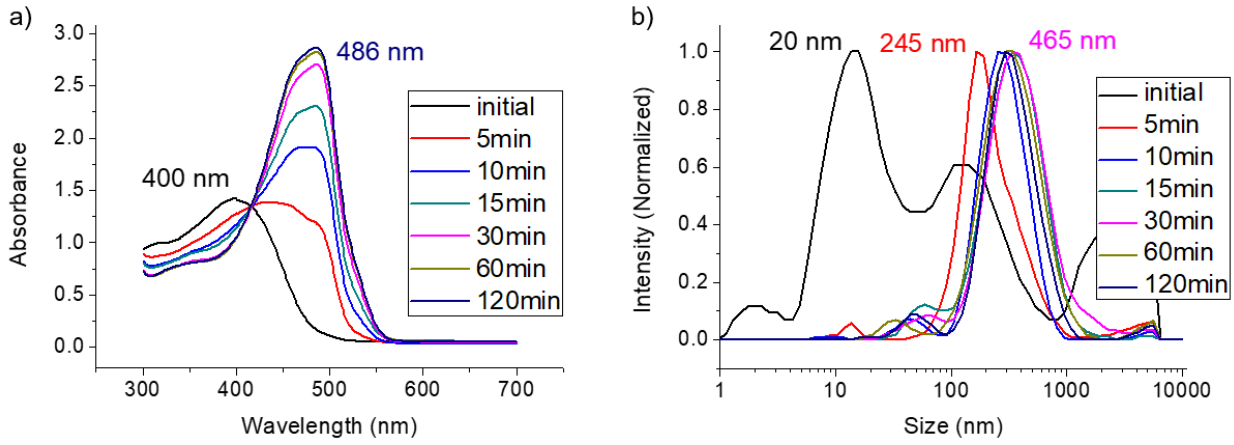


Figure S3. (a) UV/vis absorbance spectra and (b) DLS profiles of **P1b**$_{50}$-*b*-**P2**$_{15}$ at 0.1 mg/ml in THF before and after fluorescent light exposure for various times.

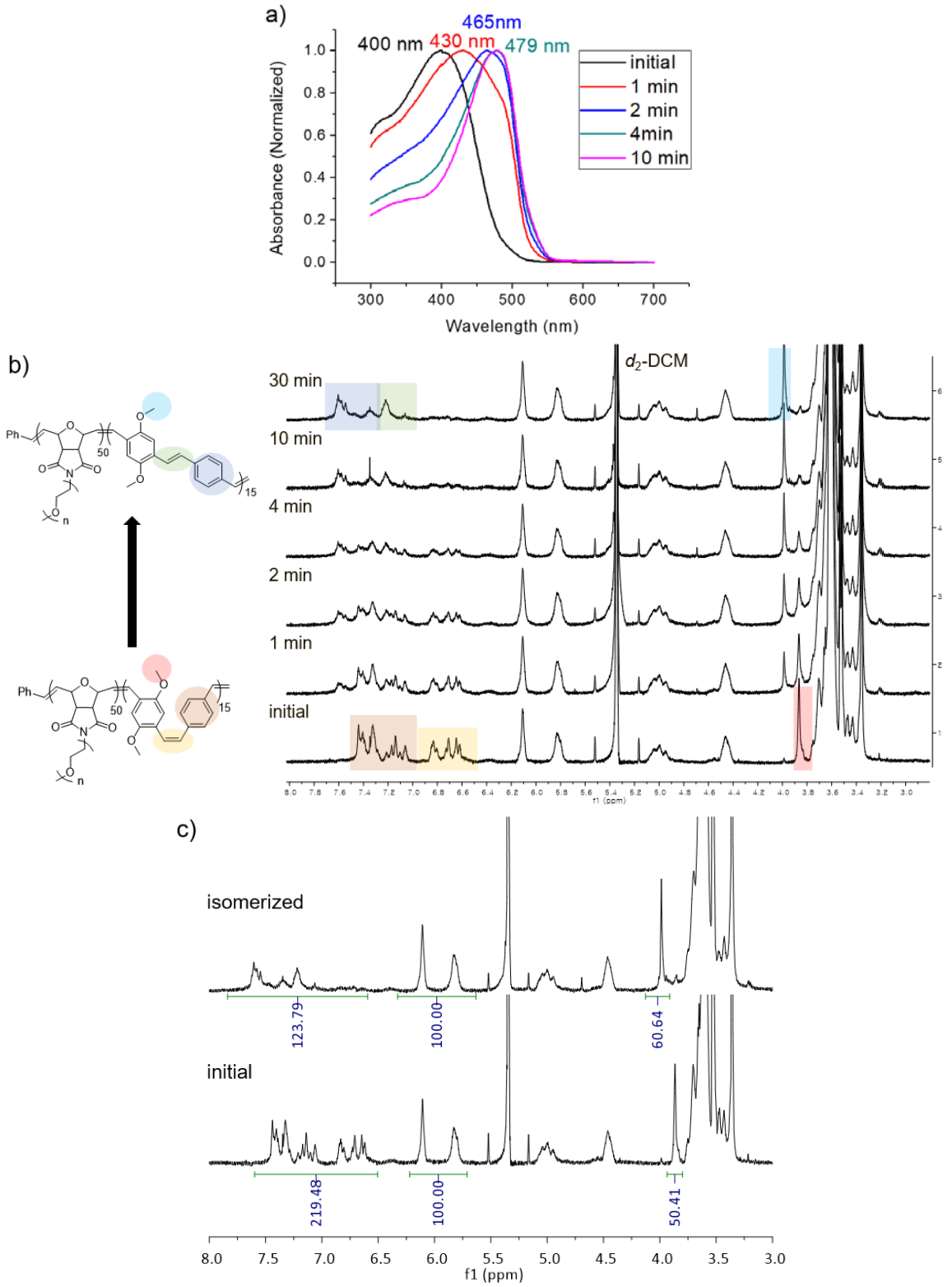


Figure S4. (a) UV/vis absorbance spectra and (b) ^{1}H NMR spectra of **P1b**$_{50}$-*b*-**P2**$_{15}$ at 0.5 mg/ml in d_2-DCM before and after LED light exposure for various times. Higher concentration of polymer requires more time for isomerization. (c) Integrated ^{1}H NMR spectra of **P1b**$_{50}$-*b*-**P2**$_{15}$ before and after isomerization in d_2-DCM. The signal from methoxy group on *cis*-rich **P2**$_{15}$ at 3.87 ppm indicates only half amount, and another half is overlapped with strong signal from PEG.

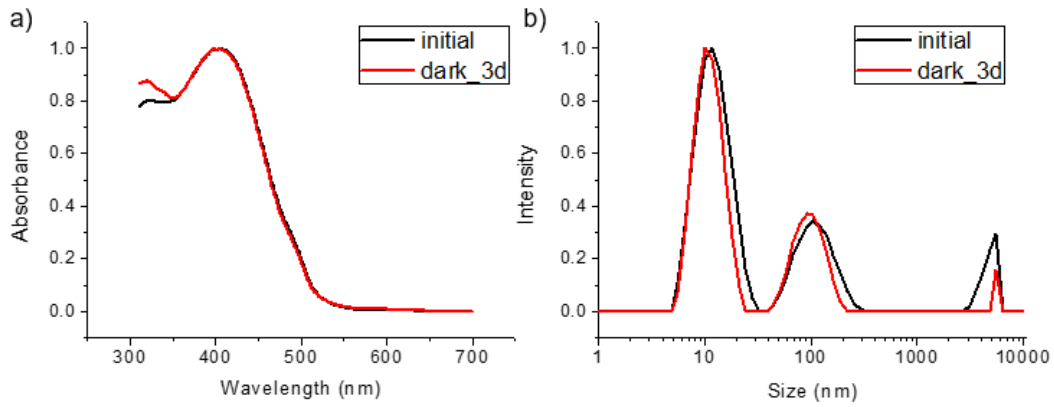


Figure S5. (a) UV/vis absorbance spectra and (b) DLS profiles of **P1b**$_{50}$-*b*-**P2**$_{15}$ at 0.1 mg/ml in THF before and after 3 days aging without light.

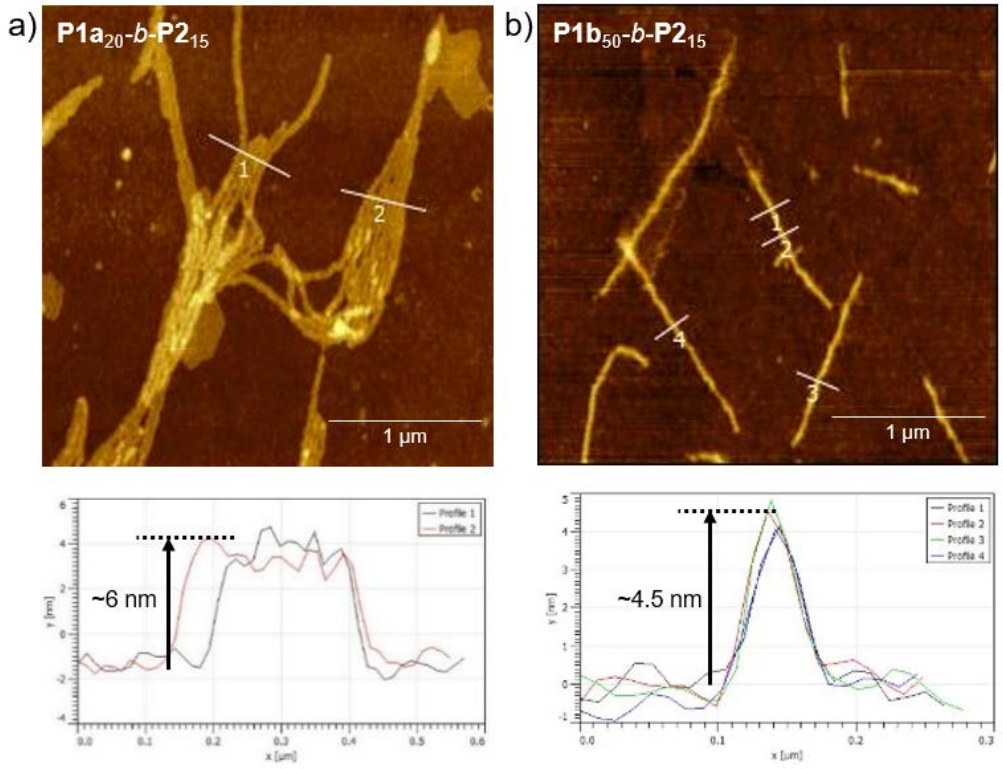


Figure S6. AFM images of (a) **P1a**$_{20}$-*b*-**P2**$_{15}$ and (b) **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by LI-CDSA. Images at bottom are height profiles along the white lines shown in top in the upper images.

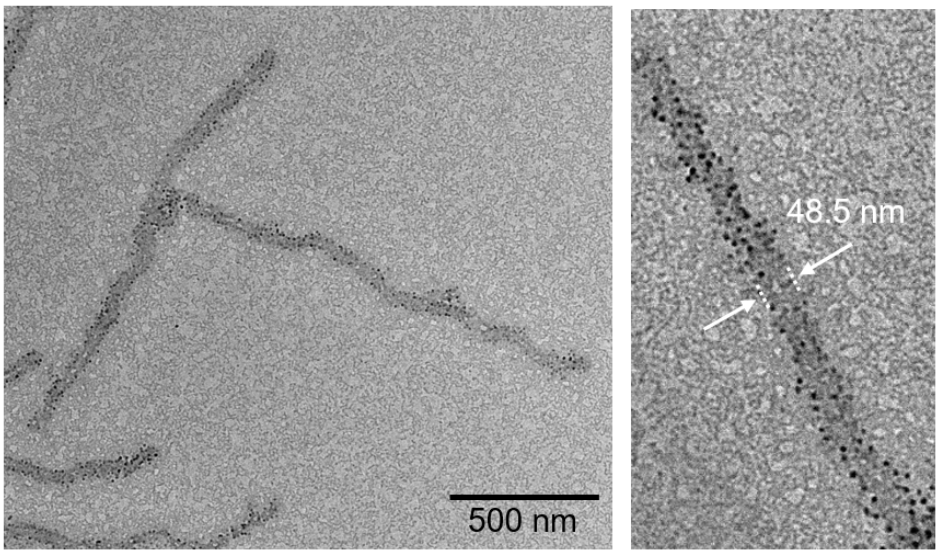


Figure S7. TEM images of nanofibers composed of isomerized **P1b**$_{50}$-*b*-**P2**$_{15}$ after selective staining of PEG group using aqueous solution of phosphotungstic acid (1 mg/ml).

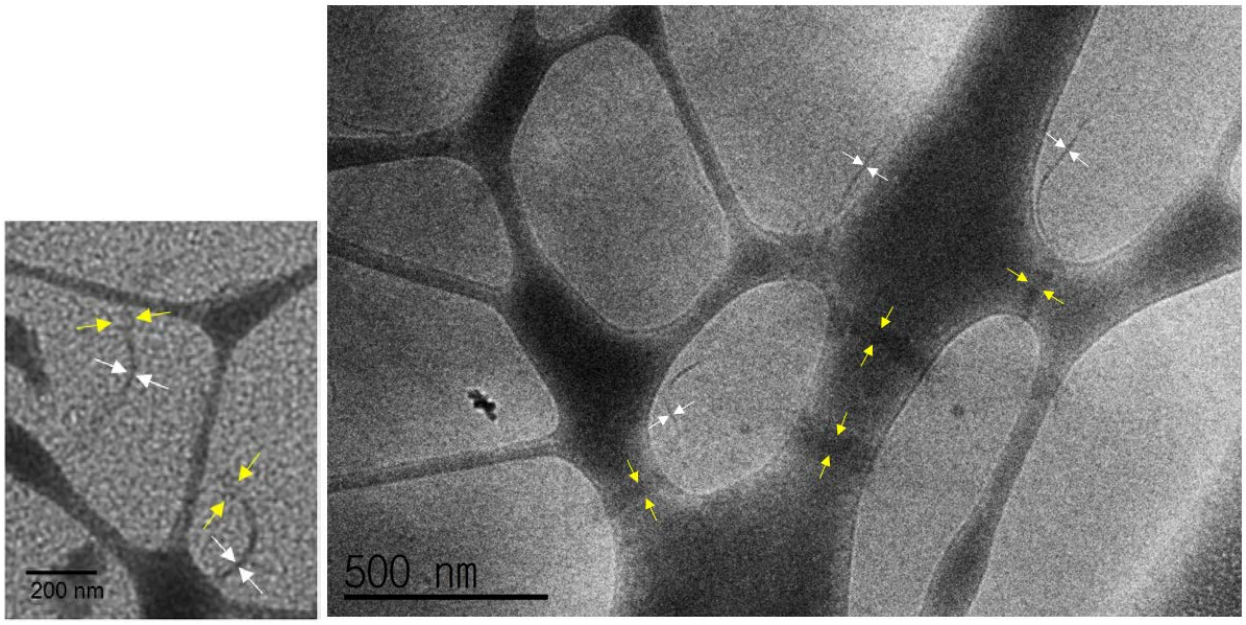


Figure S8. Cryo-TEM images of nanofibers composed of isomerized **P1b**$_{50}$-*b*-**P2**$_{15}$ in THF at 0.03 mg/ml. White arrows indicate thinner parts (height of ribbons) and yellow arrows indicate thicker parts (width of ribbons).

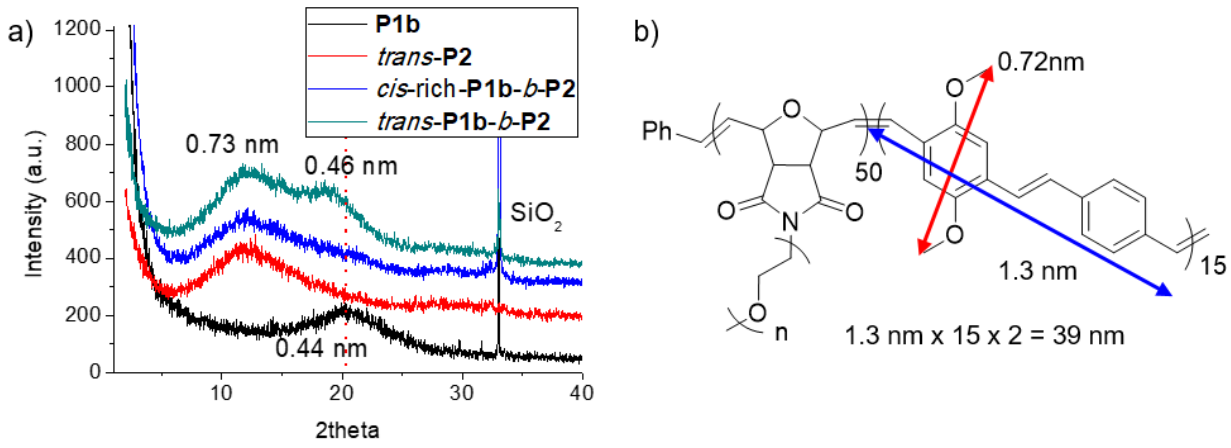


Figure S9. (a) Film XRD spectra of **P1b**$_{50}$ (black), isomerized *trans*-**P2**$_{15}$ (red), initial *cis*-rich-**P1b**$_{50}$-*b*-**P2**$_{15}$ (blue) and isomerized *trans*-**P1b**$_{50}$-*b*-**P2**$_{15}$ (green). Dotted red line indicates signal from the **P1b** first block, which is different from signal of *trans*-**P1b**$_{50}$-*b*-**P2**$_{15}$. All samples were prepared by drop casting of polymer solutions (10 mg/ml, THF) on SiO_2 wafer. (b) Unit lengths of **P2**$_{15}$ calculated by Chem3D program (Cambridge soft).

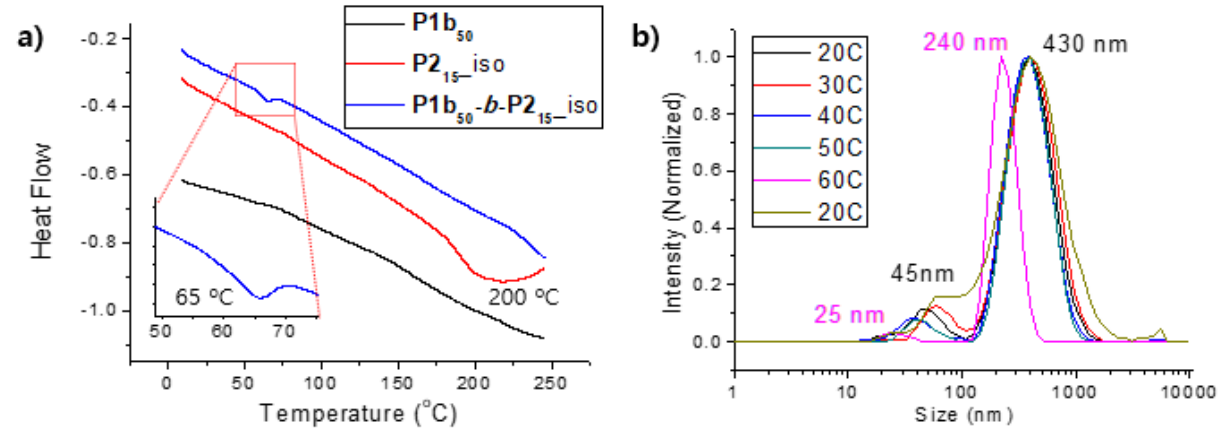


Figure S10. (a) DSC profiles of of **P1b**$_{50}$ (black line), isomerized *trans*-**P2**$_{15}$ (red line), and isomerized *trans*-**P1b**$_{50}$-*b*-**P2**$_{15}$ (blue line). (b) DLS profiles of isomerized **P1b**$_{50}$-*b*-**P2**$_{15}$ at 0.1 mg/ml in THF at different temperatures.

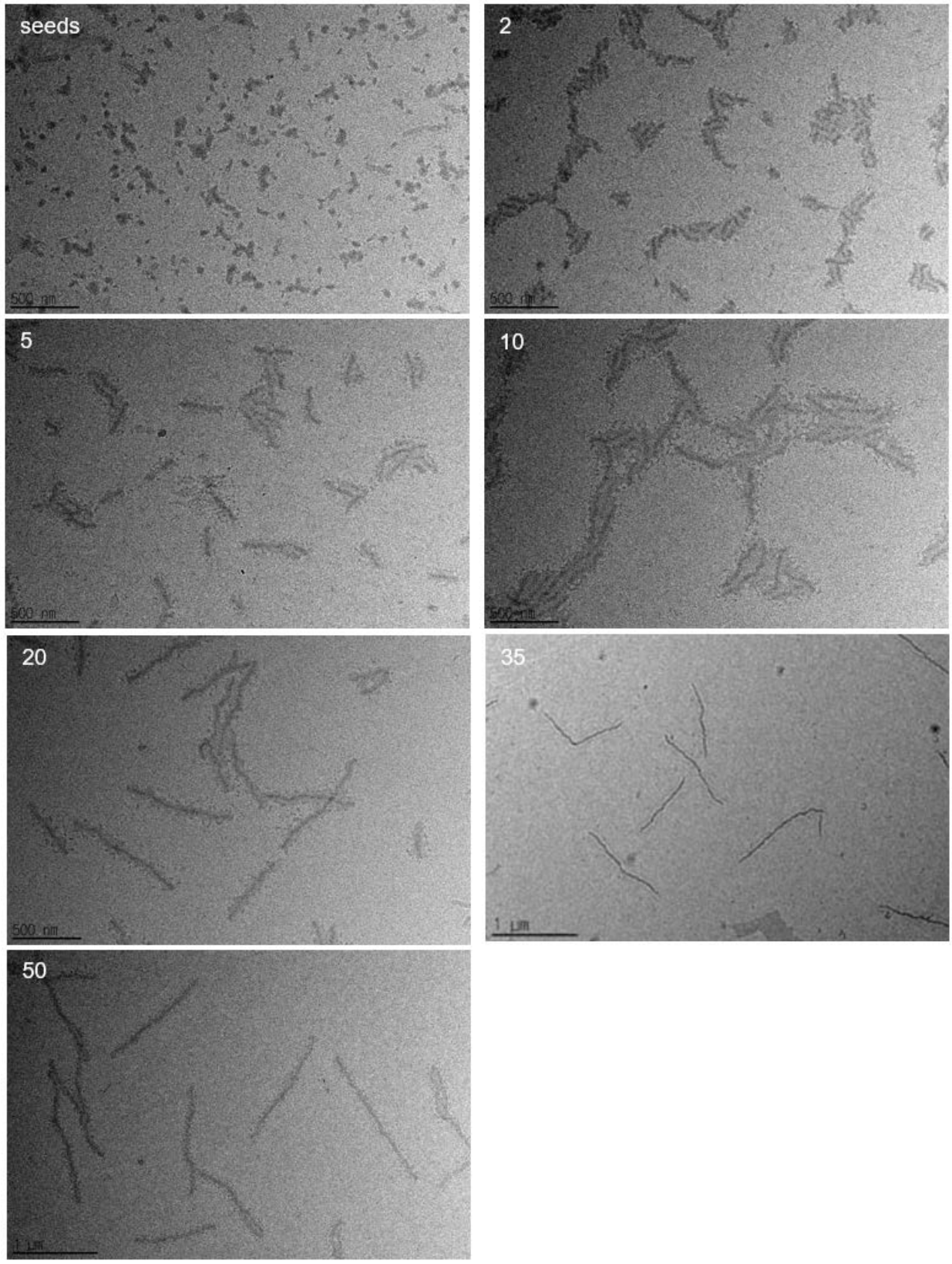
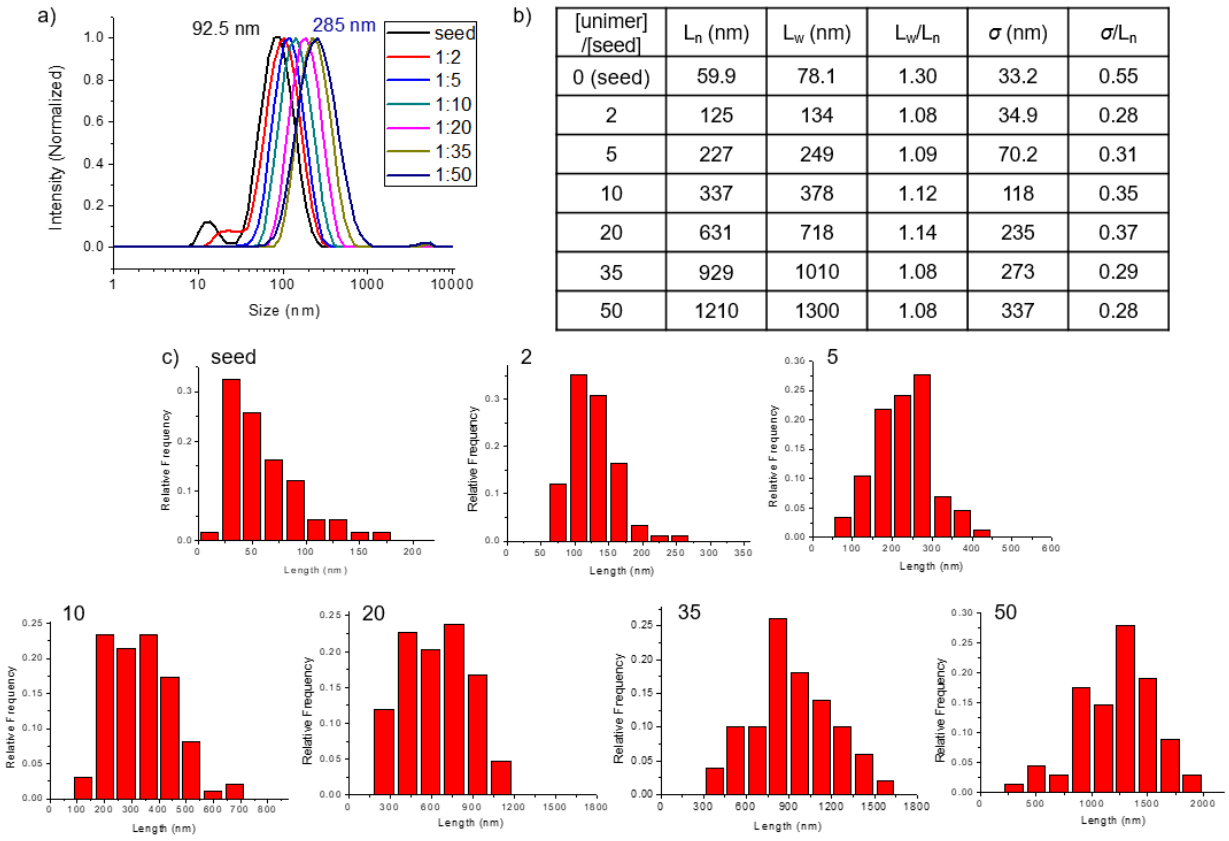


Figure S11. TEM images of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20, 35 and 50 by LED irradiation to THF solutions (0.1 mg/ml) at room temperature.



[unimer] /[seed]	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
0 (seed)	59.9	78.1	1.30	33.2	0.55
2	125	134	1.08	34.9	0.28
5	227	249	1.09	70.2	0.31
10	337	378	1.12	118	0.35
20	631	718	1.14	235	0.37
35	929	1010	1.08	273	0.29
50	1210	1300	1.08	337	0.28

Figure S12. (a) DLS profiles, (b) table and (c) distribution histograms of contour length analysis of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20, 35 and 50 by LED irradiation to THF solutions (0.1 mg/ml) at room temperature.

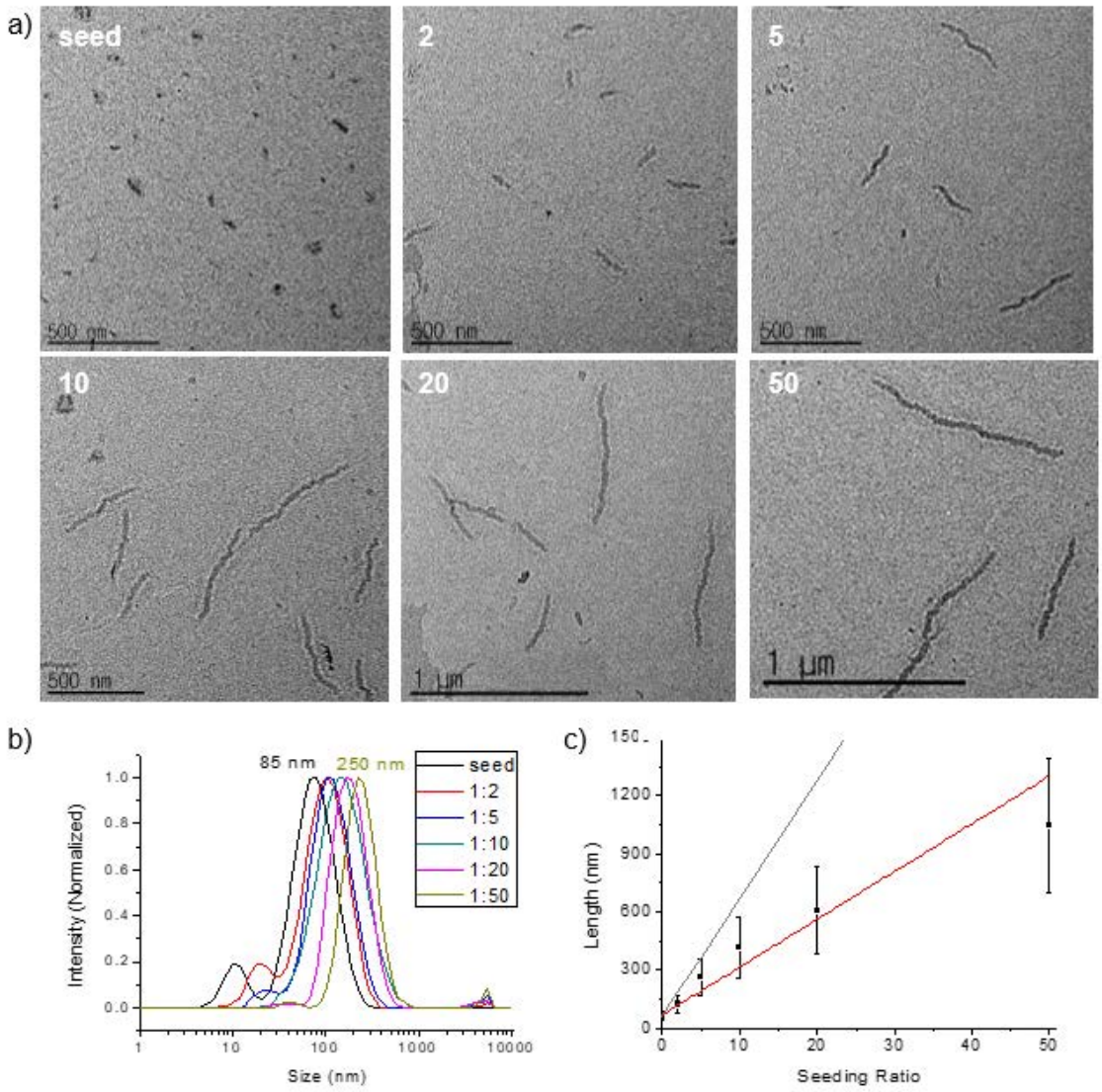


Figure S13. (a) TEM images, (b) DLS profiles and (c) plot of L_n values versus unimer-to-seed ratio of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by 1 hour of fluorescent light irradiation to THF solutions (0.1 mg/ml) at 10 °C. Error bars indicate standard deviation (σ) and the solid gray line and red line represent theoretical L_n values and linear plot of experimental L_n values, respectively.

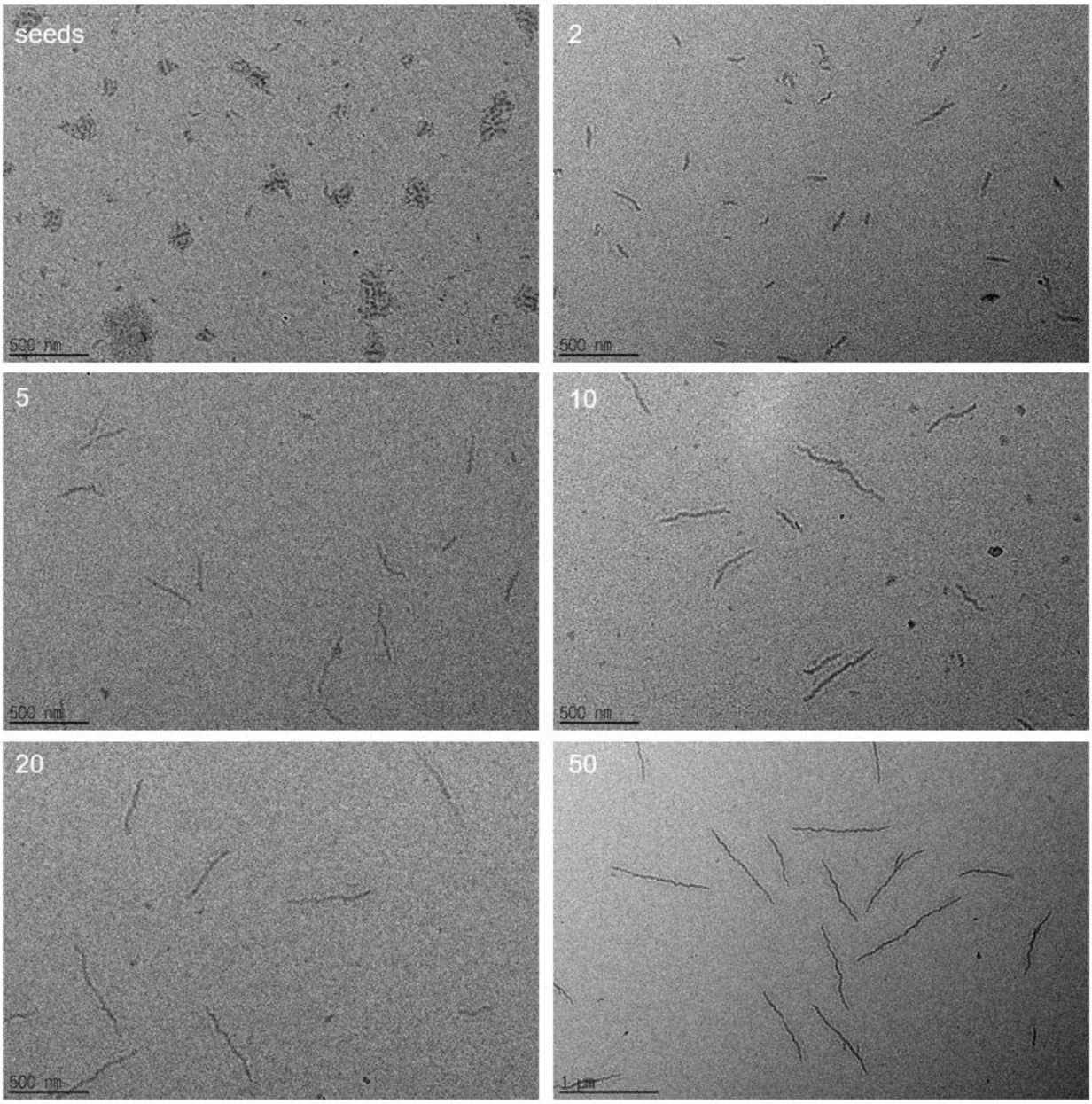


Figure S14. TEM images of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by fluorescent light irradiation to THF solutions (0.1 mg/ml) at 10 ^{o}C.

a)

[unimer] /[seed]	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
0 (seed)	60.8	69.6	1.15	23.4	0.39
2	123	140	1.13	45.5	0.37
5	262	294	1.12	92.9	0.35
10	415	475	1.14	158	0.38
20	608	688	1.13	222	0.37
50	1050	1160	1.11	348	0.33

b)

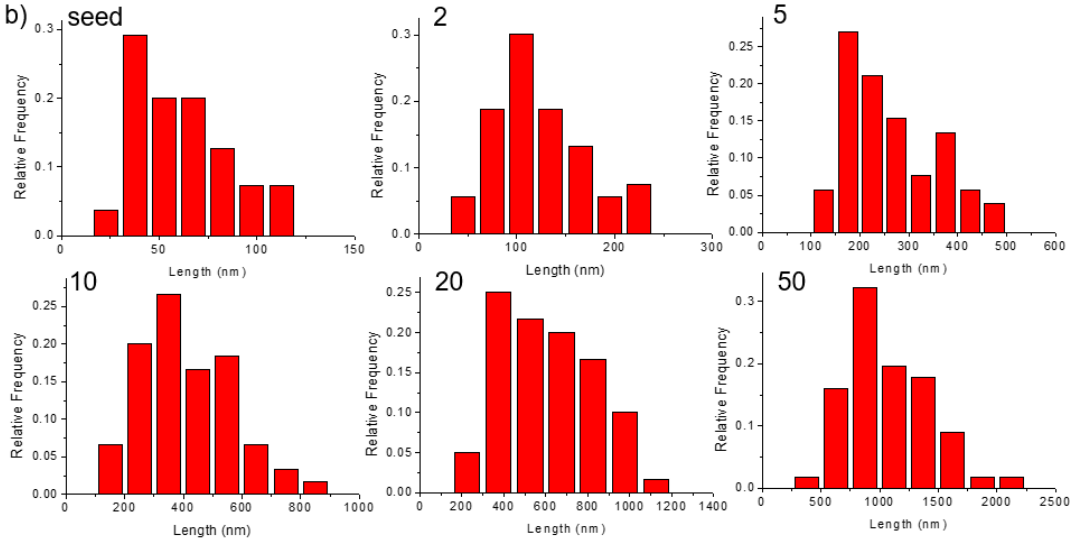


Figure S15. (a) Table and (b) distribution histograms of contour length analysis of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by fluorescent light irradiation to THF solutions (0.1 mg/ml) at 10 °C.

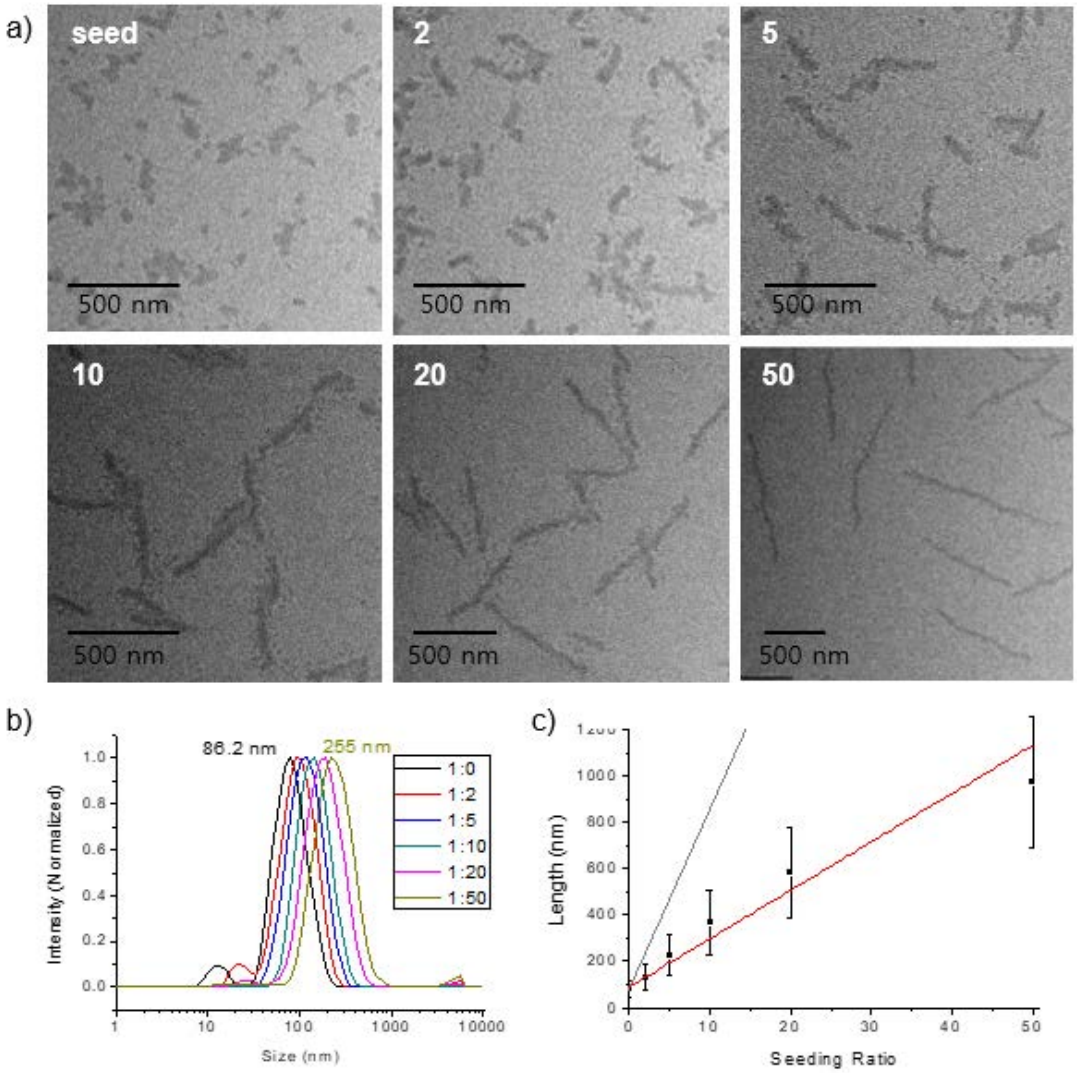


Figure S16. (a) TEM images, (b) DLS profiles and (c) plot of L_n values versus unimer-to-seed ratio of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by 5 minutes of LED irradiation to THF solutions (0.1 mg/ml) at 10 °C. Error bars indicate standard deviation (σ) and the solid gray line and red line represent theoretical L_n values and linear plot of experimental L_n values, respectively.

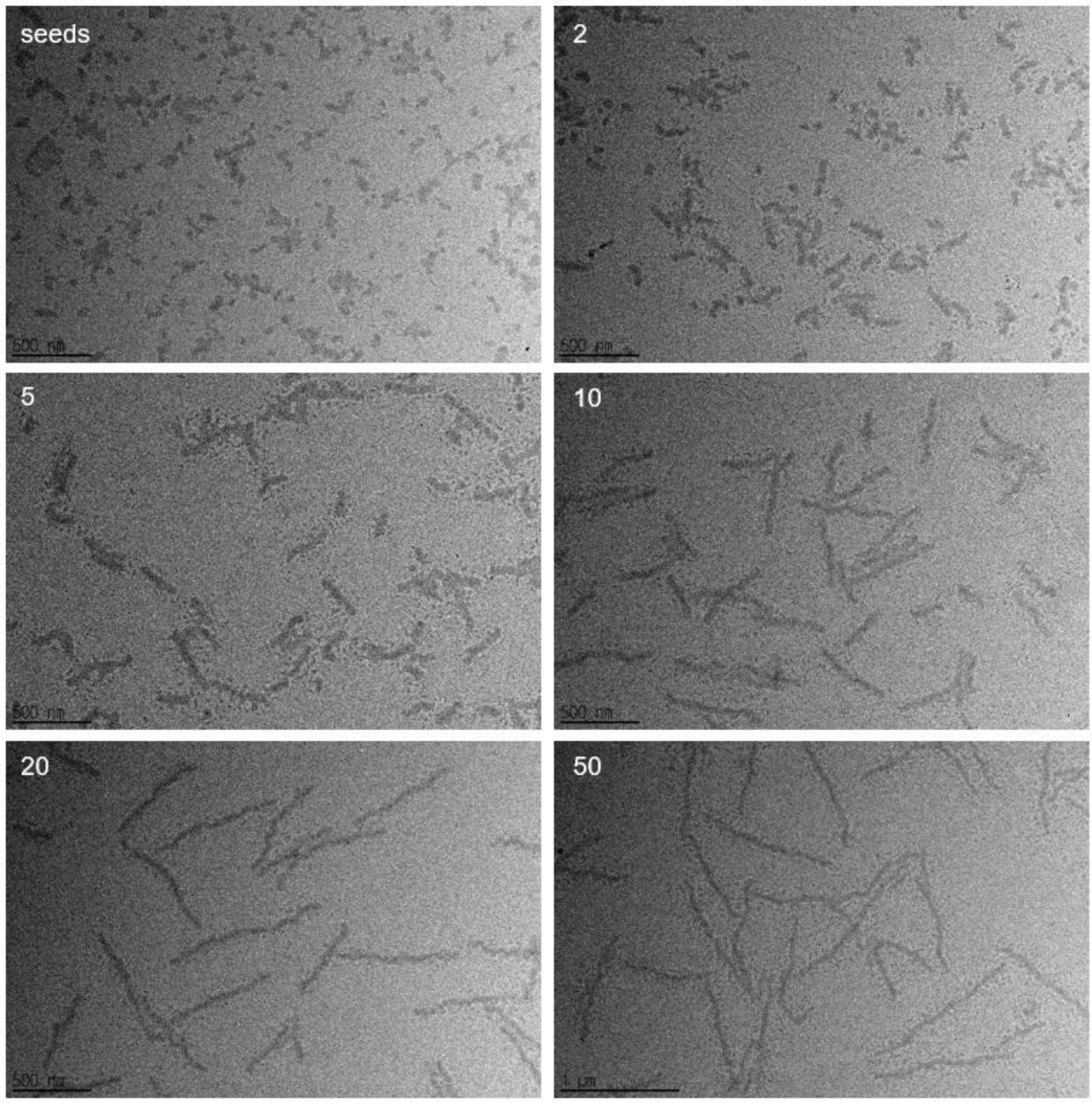


Figure S17. TEM images of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by LED irradiation to THF solutions (0.1 mg/ml) at 10 ^{o}C.

a)

[unimer] /[seed]	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
0 (seed)	77.7	94.2	1.21	35.9	0.46
2	132	156	1.19	57.2	0.43
5	227	261	1.15	88.7	0.39
10	371	423	1.14	139	0.37
20	585	648	1.11	194	0.33
50	973	1050	1.08	281	0.29

b)

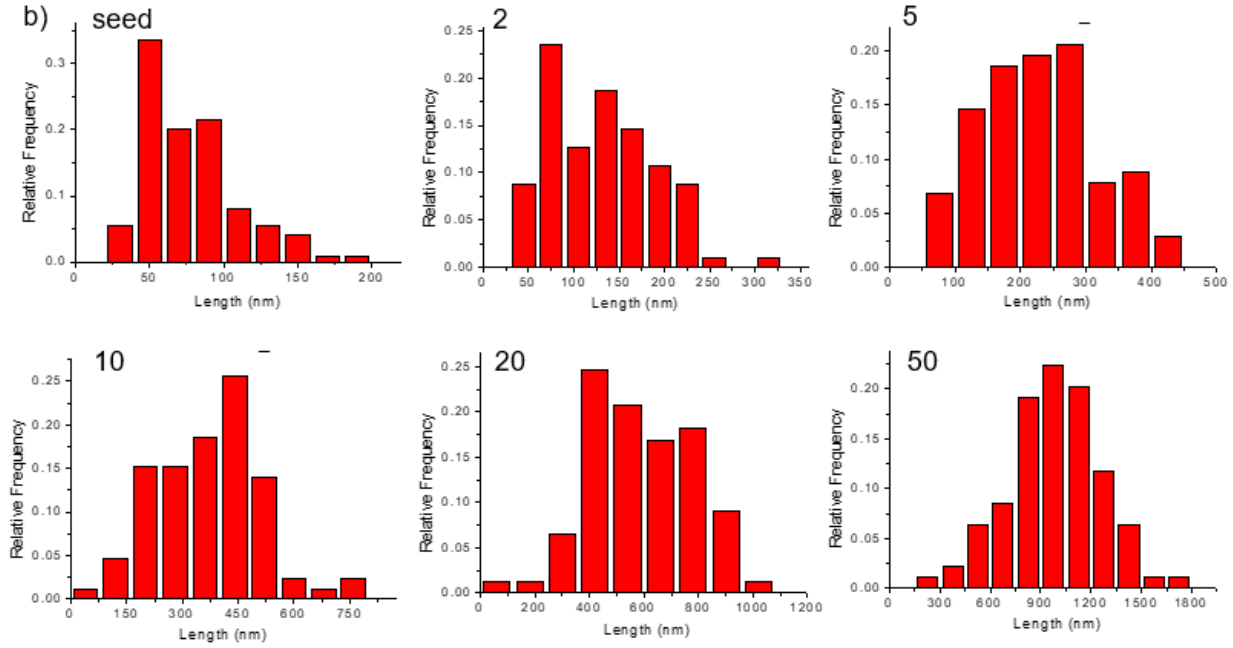


Figure S18. (a) Table and (b) distribution histograms of contour length analysis of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by LED irradiation to THF solutions (0.1 mg/ml) at 10 °C.

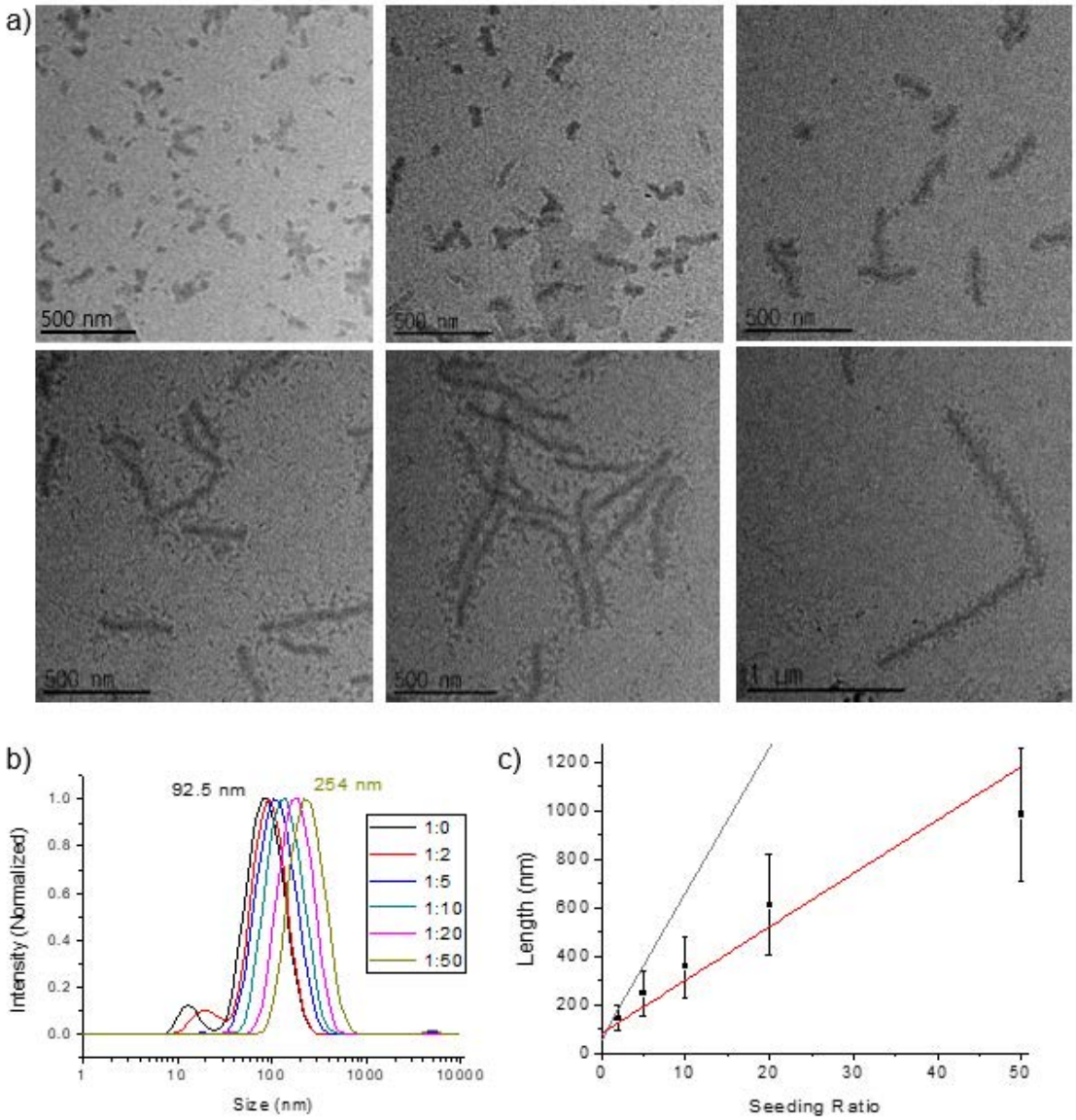


Figure S19. (a) TEM images, (b) DLS profiles and (c) plot of L_n values versus unimer-to-seed ratio of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by 1 hour of fluorescent light irradiation to THF solutions (0.1 mg/ml) at 30 °C. Error bars indicate standard deviation (σ) and the solid gray line and red line represent theoretical L_n values and linear plot of experimental L_n values, respectively.

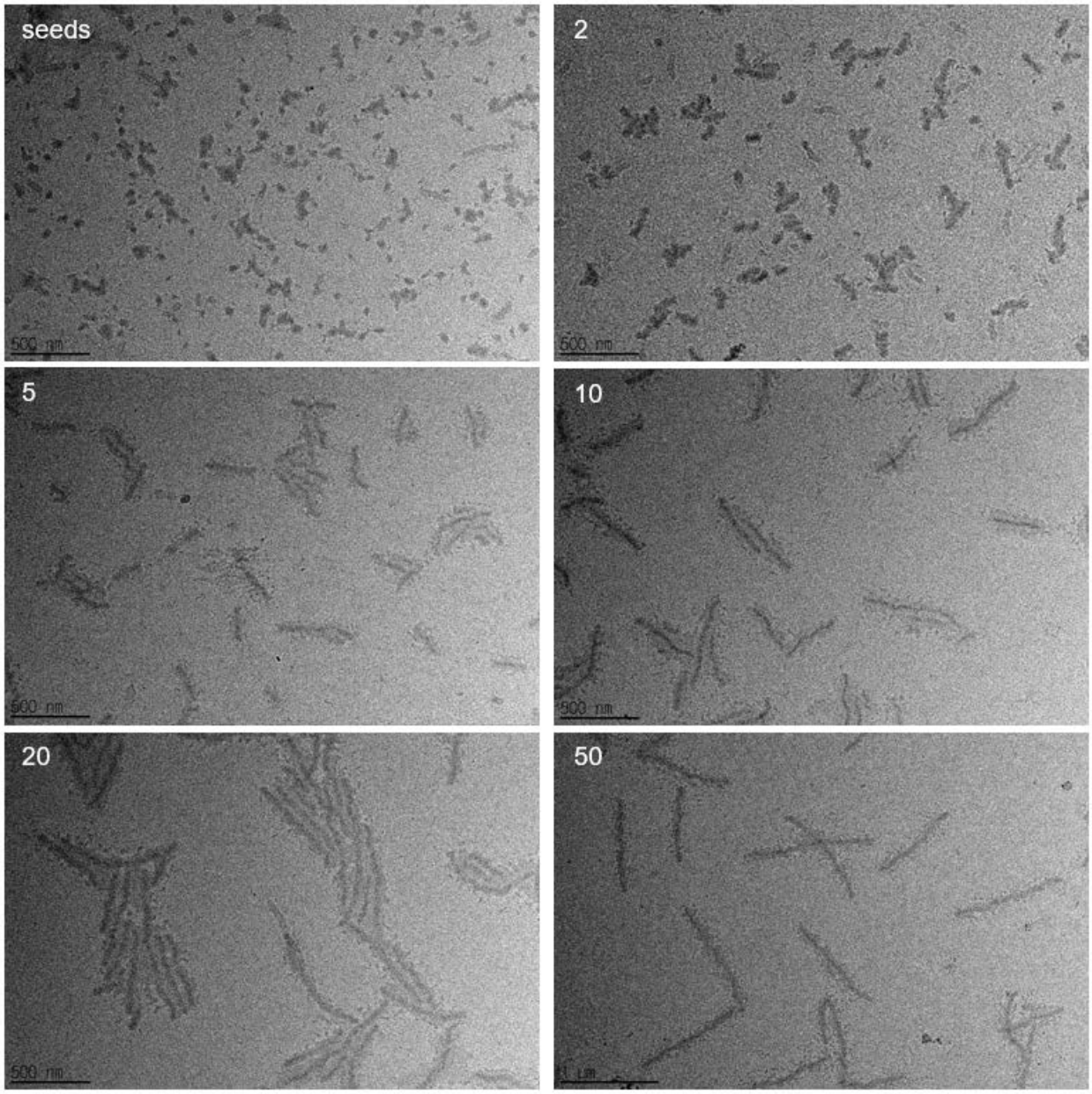


Figure S20. TEM images of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by fluorescent light irradiation to THF solutions (0.1 mg/ml) at 30 ^{o}C.

a)

[unimer] /[seed]	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
0 (seed)	59.9	78.1	1.30	33.2	0.55
2	145	164	1.13	53.2	0.37
5	248	281	1.14	91.9	0.37
10	356	399	1.12	125	0.35
20	611	681	1.11	207	0.34
50	985	1060	1.08	277	0.28

b)

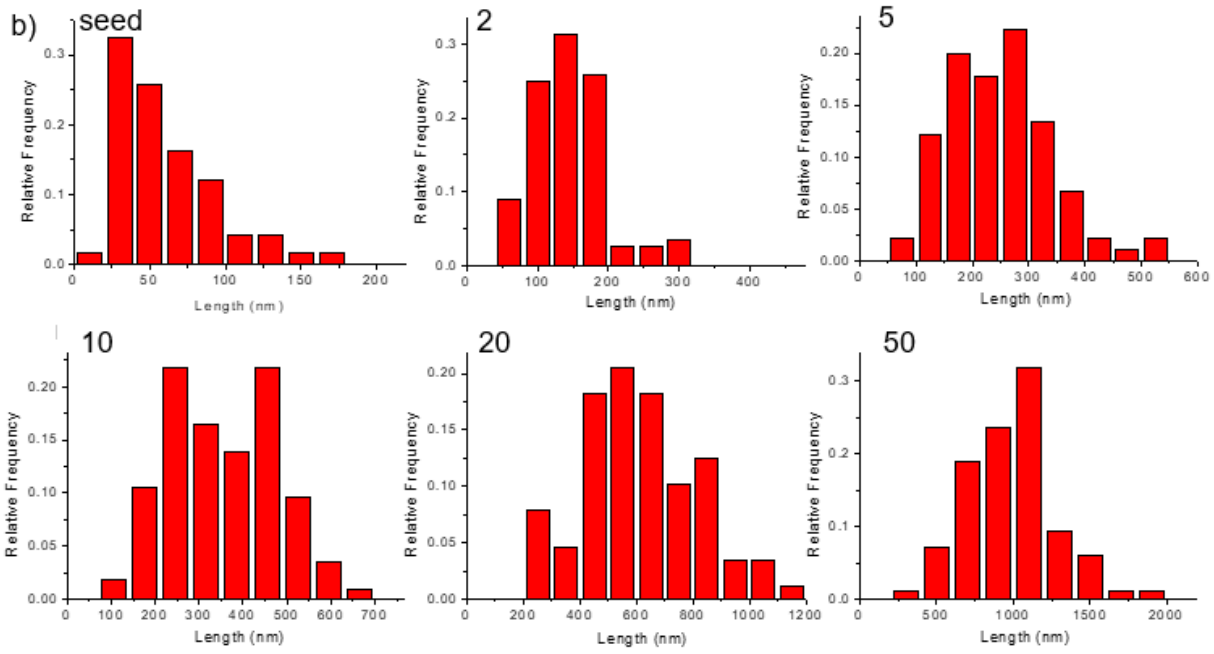


Figure S21. (a) Table and (b) distribution histograms of contour length analysis of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio from 2 to 5, 10, 20 and 50 by fluorescent light irradiation to THF solutions (0.1 mg/ml) at 30 ºC.

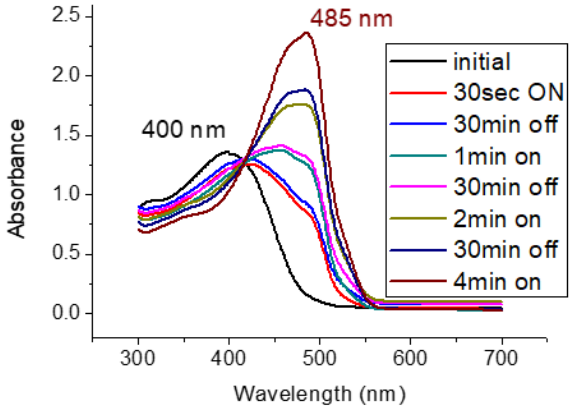


Figure S22. UV/vis spectra of **P1b**$_{50}$-*b*-**P2**$_{15}$ measured during light-on-off cycles.

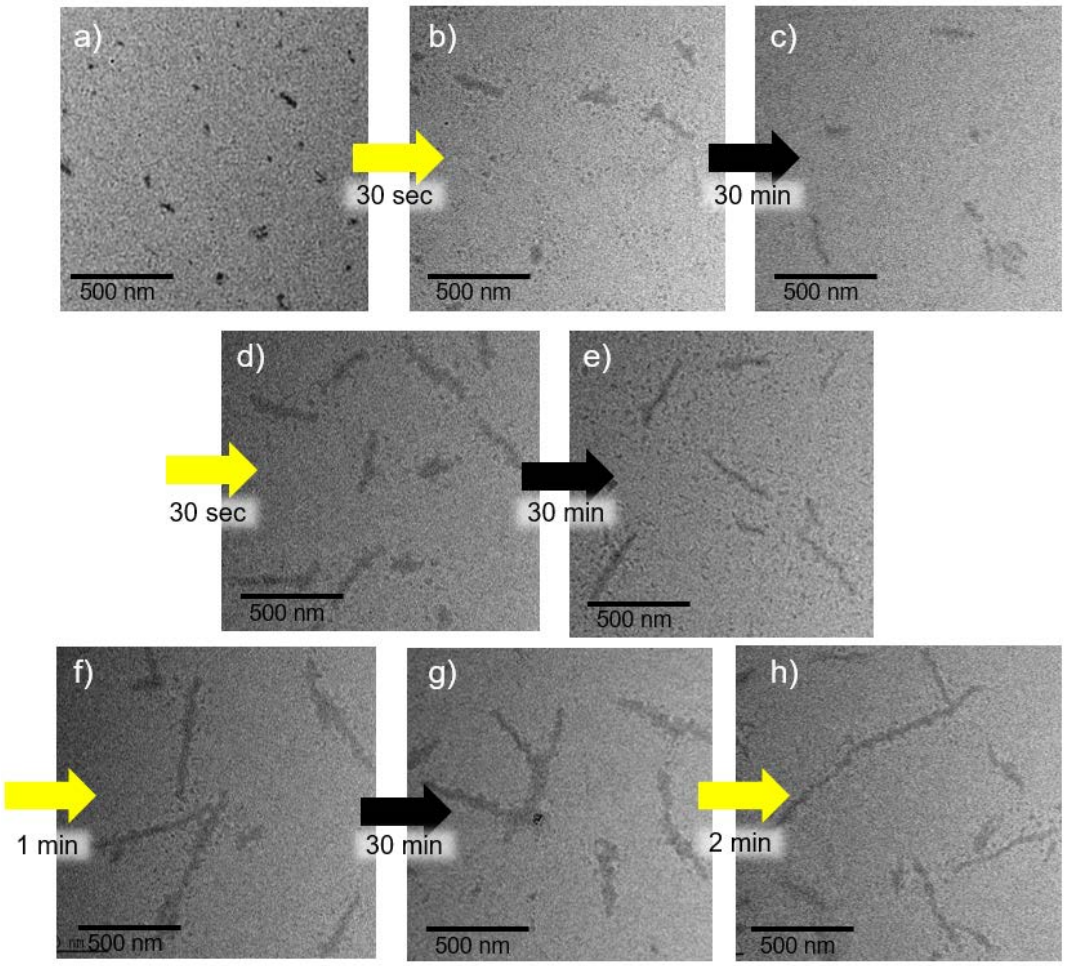


Figure S23. TEM images of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio of 50 under LED on-off cycles. (a) initial seed micelles, (b) 30 sec irradiation, (c) 30 min at dark, (d) additional 30 sec irradiation, (e) 30 min at dark, (f) additional 1 min irradiation, (g) 30 min at dark, and (h) additional 2 min irradiation. Yellow arrows indicated LED irradiation and block arrows indicated absence of light.

a)

On-off time (min)	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
0 (seed)	77.7	94.2	1.21	35.9	0.46
0.5 (ON)	158	189	1.20	70.3	0.45
30 (OFF)	164	197	1.20	74.5	0.45
0.5 (ON)	299	346	1.16	120	0.40
30 (OFF)	289	344	1.19	127	0.44
1.0 (ON)	490	577	1.18	208	0.42
30 (OFF)	482	548	1.14	179	0.37
2.0 (ON)	692	826	1.19	308	0.44

b)

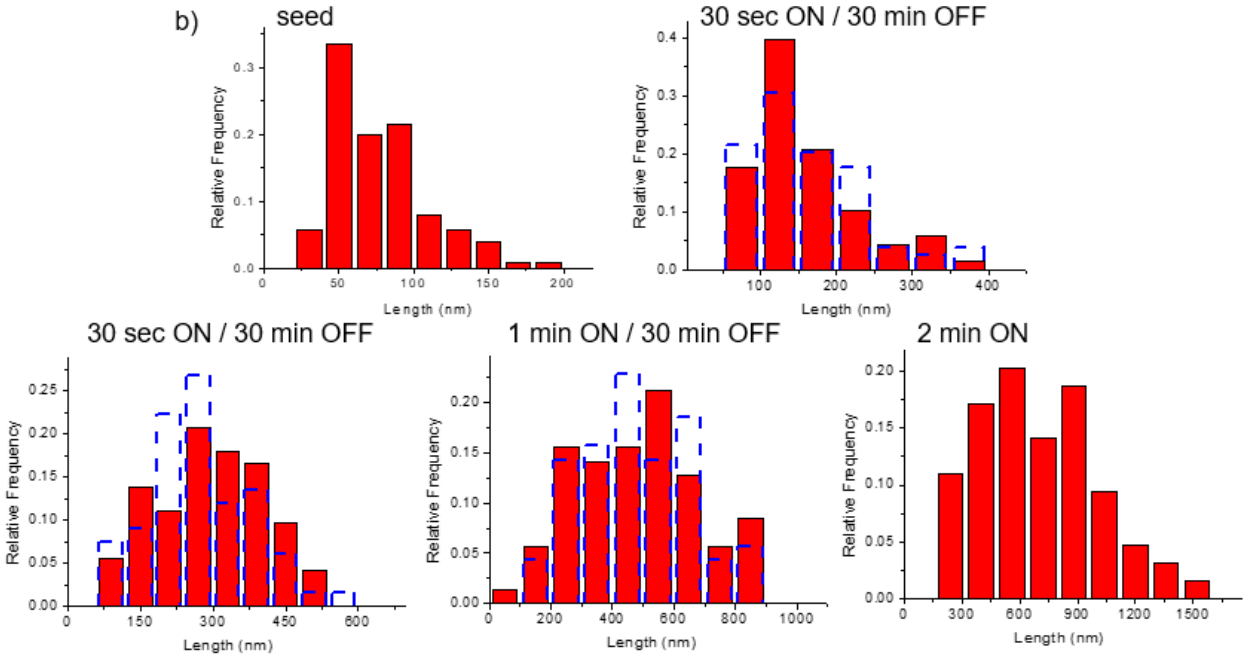


Figure S24. (a) Table and (b) distribution histograms of contour length analysis of **P1b**$_{50}$-*b*-**P2**$_{15}$ nanofibers prepared by seeded growth using unimer-to-seed ratio of 50 under LED on-off cycles. Red boxes indicated distributions of nanofibers after LED irradiation and empty dashed boxes indicated those after 30 minutes aging at dark.

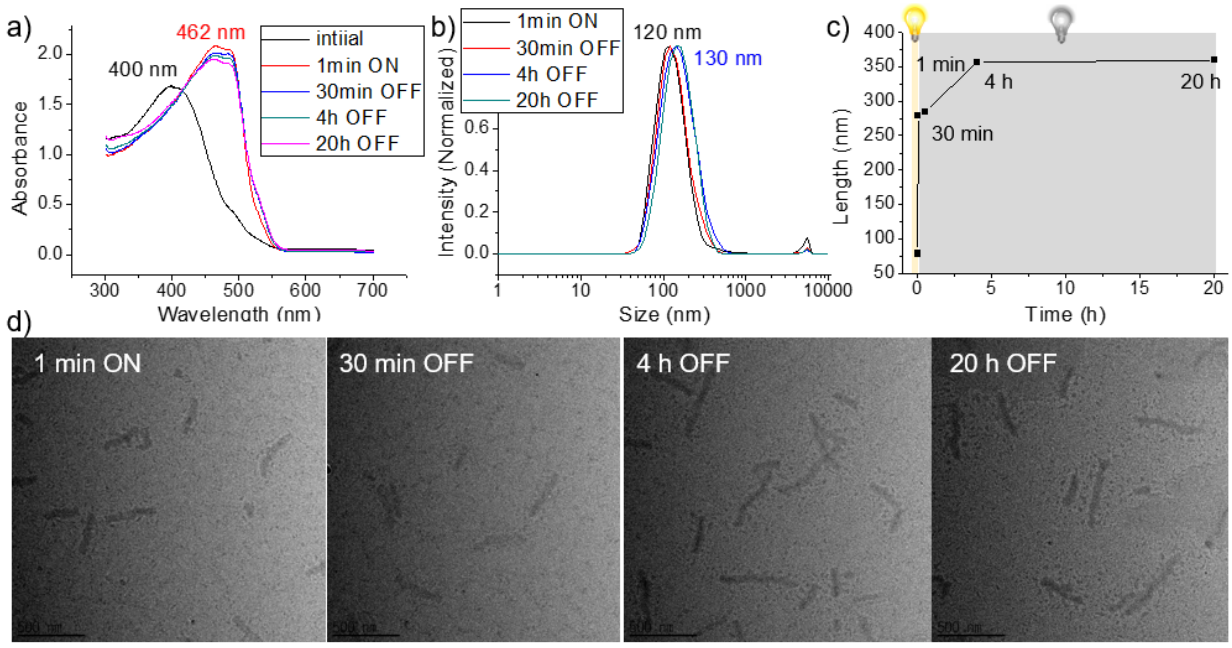
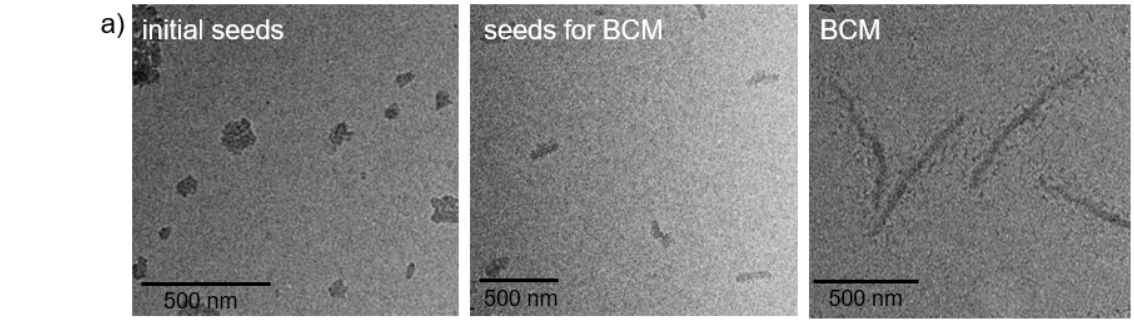


Figure S25. Various analysis of **P1b**$_{50}$-*b*-**P2**$_{15}$ in THF after LED irradiation for 1 minutes followed by long-term aging without light. (a) UV/vis spectra, (b) DLS profiles, (c) Plot of L_n versus time (yellow regions: light on, gray region: light off) and (d) TEM images. The slow growth of nanofibers at dark condition supports that partially isomerized BCPs had much slower self-assembly rate which could be seen as trapped or deactivated for short period time as 30 minutes. This result could support that rate of self-assembly could be controlled by the level of isomerization, and this enabled controlling the growth of nanofibers by light on-and-off in relatively short period of time.



b)

	L_n (nm)	L_w (nm)	L_w/L_n	σ (nm)	σ/L_n
initial seeds	68.7	77.4	1.13	24.5	0.36
seeds for BCM	218	255	1.17	90.7	0.42
center of BCM	225	304	1.35	135	0.60
BCM	802	841	1.05	179	0.22

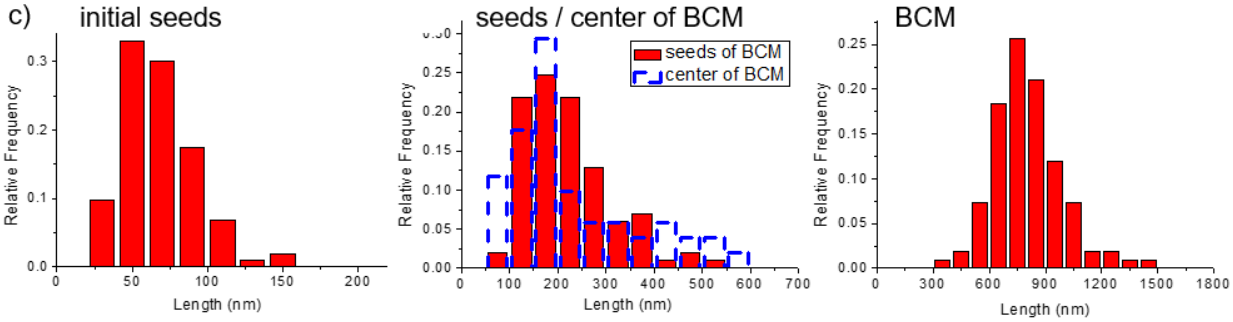


Figure S26. (a) TEM images, (b) table, and (c) distribution histograms of contour length analysis of ABA triblock comicelles (BCM) prepared by seeded growth of **P1b**$_{50}$-*b*-**P2**$_{15}$ (A) from **P1a**$_{20}$-*b*-**P2**$_{15}$ (B) seed micelles. **P1a**$_{20}$-*b*-**P2**$_{15}$ seed micelles were prepared by seeded growth from the initial seeds using unimer-to-seed ratio of 2.

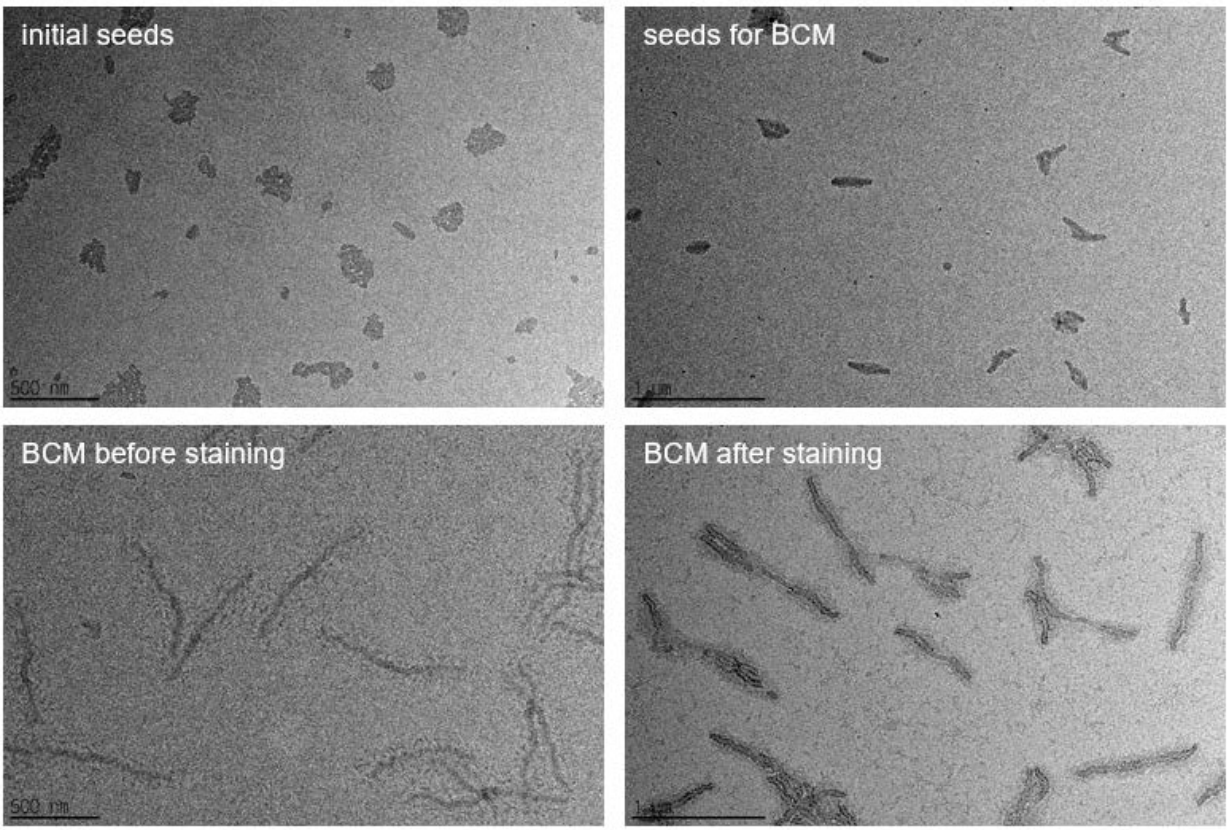


Figure S27. TEM images of initial seeds, seeds for BCM and BCM prepared by seeded growth of **P1b**$_{50}$-*b*-**P2**$_{15}$ from **P1a**$_{20}$-*b*-**P2**$_{15}$. For selective staining of **P1b**$_{50}$, phosphotungstic acid was used.

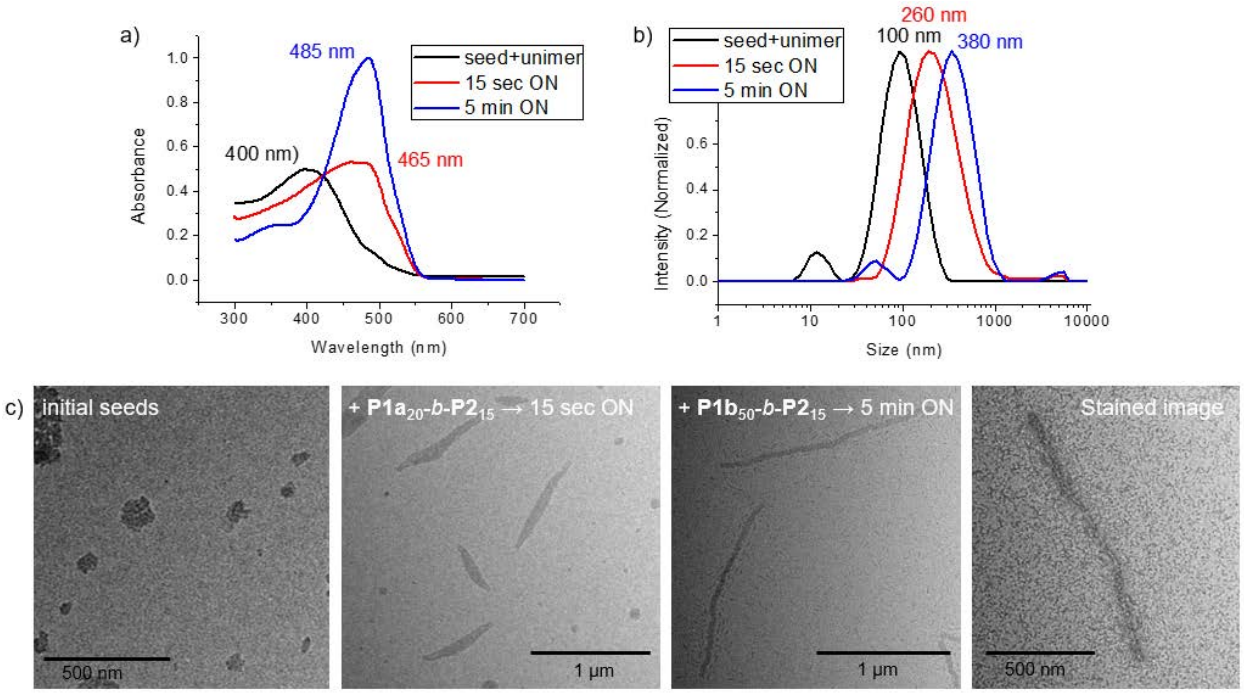


Figure S28. (a) UV/vis absorbance spectra, (b) DLS profiles, and (c) TEM images of each step of gradient comicelle preparation. 10 equivalents of **P1a**$_{20}$-*b*-**P2**$_{15}$ were added to seed micelles of **P1a**$_{20}$-*b*-**P2**$_{15}$ following partial photoisomerization by 15 sec LED irradiation. Then another 10 equivalents of **P1b**$_{50}$-*b*-**P2**$_{15}$ were added and the mixture of BCPs was fully isomerized by 5 min LED irradiation. The concentration of solution was maintained as 0.1 mg/ml in THF. For selective staining of **P1b**$_{50}$, phosphotungstic acid was used.

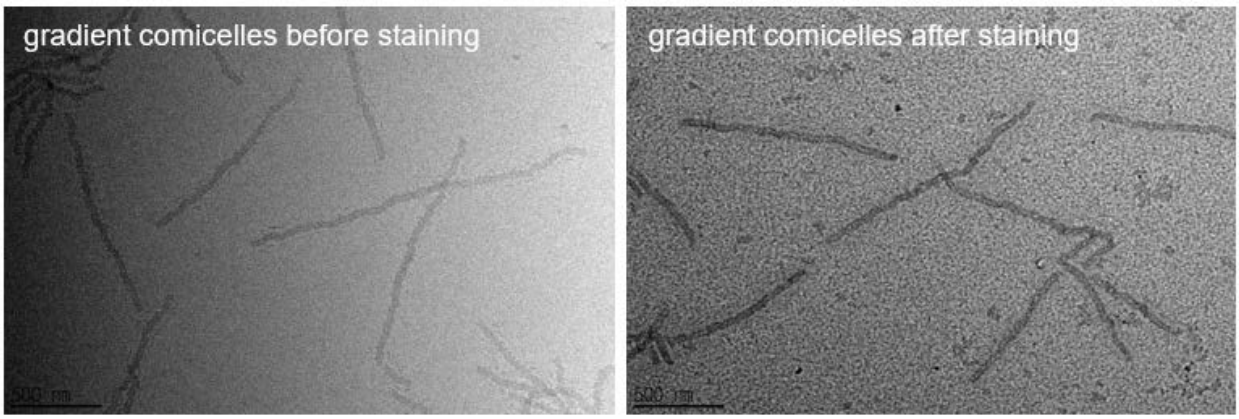


Figure S29. TEM images of gradient comicelles before and after staining. For selective staining of **P1b**$_{50}$, phosphotungstic acid was used.

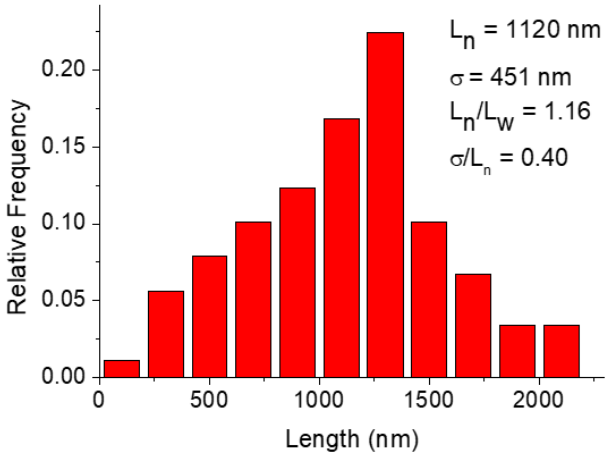


Figure S30. Contour length distribution of gradient comicelles.

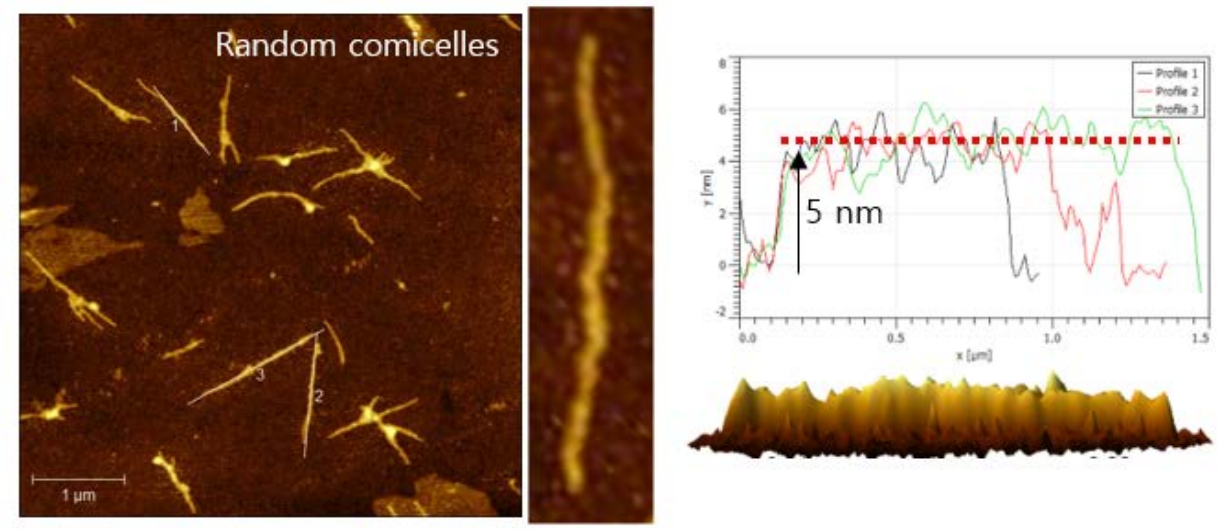
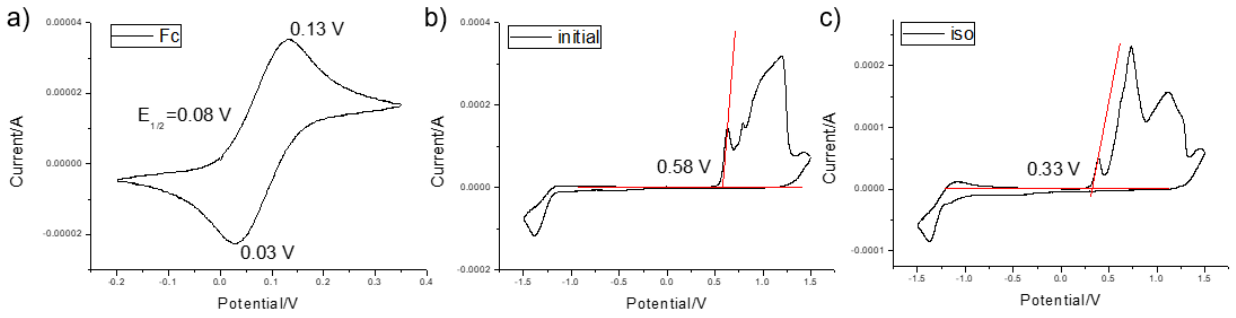


Figure S31. AFM images of random comicelles. Top left: full scale image, middle: magnified image of an individual random comicelle, right top: overlay of the height profiles along the white lines shown in the full-scale image, and right bottom: 3D image.



d)

	HOMO(eV)	LUMO(eV)	E_{opt} (eV)
Initial	- 5.30	- 2.72	2.58
isomerized	- 5.05	- 2.80	2.25

Figure S32. Cyclic voltammograms of (a) ferrocene standard (1 mM in acetonitrile) and (b-c) **P1a**$_{50}$-*b*-**P2**$_{20}$ before and after isomerization, respectively. The spectrum was measured from polymer film on the glassy carbon working electrode prepared by drop casting of the polymer solution with the concentration of 5 mg/ml. Ag/Ag+ (0.1M $AgNO_3$ in acetonitrile) reference electrode and platinum wire counter electrode were used at a scan rate of 100 mV/s. (d) Table of optical E_g, HOMO, and LUMO level calculated from the UV/vis spectra and CV spectra. Optical E_g was calculated from the onset point of the UV/vis spectra. HOMO = -4.8-($E_{ox,onset}$-$Fc^{1/2}$). [c]LUMO = HOMO + optical E_g

References

1. Contreras, A. P.; Tlenkopatchev, M. A.; del Mar López-González, M.; Riande, E. *Macromolecules* **2002,** *35*, (12), 4677-4684.

2. Menk, F.; Shin, S.; Kim, K.-O.; Scherer, M.; Gehrig, D.; Laquai, F.; Choi, T.-L.; Zentel, R. *Macromolecules* **2016,** *49*, (6), 2085-2095.

3. Shin, S.; Gu, M.-L.; Yu, C.-Y.; Jeon, J.; Lee, E.; Choi, T.-L. *J. Am. Chem. Soc.* **2018,** *140*, (1), 475-482.