# **Supporting Information**

Preparation of defect-free nanocaterpillars via in situ nanoparticlisation of well-defined polyacetylene block copolymer

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## **1. Experimental Details**

#### **General experimental**

All reactions were carried out under dry argon atmospheres using standard Schlenk-line techniques. All anhydrous deuterated solvents ( $\geq$ 99.95 %) were purchased from Euriso-Top<sup>®</sup> and were used degassed for 10 mins before polymerisation. Toluene for the monomer synthesis was obtained from solvent purification system using filtration through an alumina column. 5-norbornene-*endo*-2,3-dicarboxylic anhydride was purchased from Tokyo Chemical Industry, followed by thermal isomerisation to the *exo*-form. Cyclooctatetraene was commercially available from Alfa Aesar and was used without further purification. The third generation Grubbs catalysts **2**, **3** were prepared by the method reported.<sup>S1</sup> 4,4-dimethylbiphenyl as an internal standard for <sup>1</sup>H NMR analysis was obtained from TCI.

NMR spectra were recorded by Varian/Oxford As-500 (500 MHz for <sup>1</sup>H/125 MHz for <sup>13</sup>C) and Bruker (300 MHz for <sup>1</sup>H) spectrometers. Cross-Polarisation/Magic-Angle-Spinning (CP/MAS) <sup>13</sup>C solid-state NMR spectroscopy analysis was performed by National Instrumentation Center for Environmental Management (NICEM) at SNU using Bruker Avance 400 WB (Magic angle spinning at 11 kHz). UV/Vis spectra were obtained by Jasco Inc. UV/vis-Spectrometer V-550. IR spectra were recorded by Thermo Scientific Nicolet iS10 FT-IR spectrometer (OMNIC 8.2 software). CHCl<sub>3</sub> SEC for polymer molecular weight analysis was carried out with Waters system (515 HPLC pump and 2410 refractive refractive index detector), Acme 9000 UV/Vis detector, and Shodex GPC LF-804 column eluted CHCl<sub>3</sub> (HPLC grade, J. T. Baker). Flow rate was 0.8 mL/min and temperature of column was maintained at 35 °C. Samples in 0.5-1.0 mg/mL CHCl<sub>3</sub> were filtered by 0.45-µm PTFE filter before injection. Elemental analysis was performed by National Center for Inter-University Research Facilities at SNU using EA1112 (CE Instrument, Italy). Multimode 8 and Nanoscope-V controller (Veeco Instrument) were used for AFM imaging. JEM-2100 (JEOL) was used for transmission electron microscopy analysis. Dynamic Light Scattering (DLS) data were obtained by Malvern Zetasizer Nano ZS.

**Preparation of N-cyclohexyl-exo-norbornene-5,6-dicarboximide (1)** This monomer was prepared by slightly modified method from the previous literature.<sup>S2</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.27 (t, 2H), 3.91-3.40 (m, 1H), 3.25 (d, 2H), 2.60 (d, 2H), 2.09-2.18 (m, 2H), 1.25-1.85 (m, 10H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 178.4, 138.1, 51.8, 47.6, 45.4, 42.7, 29.0, 26.0, 25.2

Preparation of Poly(1)-block-Poly(cyclooctatetraene)(Table 1, entries 1-4)



Monomer **1** (101.30 mg, 0.4134 mmol, 50 eq.) was weighed in a 4-mL sised screw-cap vial with septum and purged with argon. Degassed anhydrous solvent was added (1.0 mL) to the vial. At room temperature, the solution of initiator **2** (6.00 mg, 1 eq.) was added (0.4 mL) to the monomer solution at once under vigorous stirring. After 20 mins, the solution of cyclooctatetraene (28  $\mu$ l, 30 eq.) was added (1.0 mL), and the mixture was stirred for 4.5-24 h at various temperatures. The reaction was quenched by excess ethyl vinyl ether at 0 °C. The crude mixture was precipitated by methanol to afford polymer PN-*b*-P(COT) as a dark powder (Yield: 87-92 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  5.76 (s, 1H), 5.45-5.50 (d, 1H), 3.88 (s, 1H), 3.28-2.67 (m, 4H), 2.16 (m, 3H), 1.81 (s, 2H) 1.65-1.55 (m, 4H), 1.30-1.20 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  178.5, 132.1, 52.6, 51.5, 50.9, 46.7-46.2, 43.0-41.0, 29.0, 26.1, 25.3 (Poly(**1**), homopolymer, has identical <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra to Poly(**1**)-*b*-Poly(COT), See Fig. S1).

#### Preparation of Poly(1)-block-Poly(cyclooctatetraene)(Table 2, entries 1-4)



Monomer **1** (101.30 mg, 0.4134 mmol, 50 eq.) was weighed in a 4-mL sized screw-cap vial with septum and purged with argon. Degassed anhydrous solvent was added (0.5 mL) to the vial. At room temperature, the solution of initiator **2** (6.00 mg, 1 eq.) or **3** (6.58 mg) was added (0.3 mL) to the monomer solution at once under vigorous stirring. After 20 mins, the solution of cyclooctatetraene (100-200 eq.) was added (0.1-0.8 mL depending on targeted [COT]), and the mixture was stirred for 12-24 h at 0 °C. The reaction was quenched by excess ethyl vinyl ether at 0 °C. The crude mixture was precipitated by methanol at 0 °C to afford polymer PN-*b*-P(COT) as a dark powder (Yield: 45-64 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  5.76 (s, 1H), 5.45-5.50 (d, 1H), 3.88 (s, 1H), 3.28-2.67 (m, 4H), 2.16 (m, 3H), 1.81 (s, 2H) 1.65-1.55 (m, 4H), 1.30-1.20 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  178.5, 132.1, 52.6, 51.5, 50.9, 46.7-46.2, 43.0-41.0,

29.0, 26.1, 25.3 (Poly(1), homopolymer, has identical <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra to Poly(1)-*b*-Poly(COT)).

<sup>1</sup>H NMR Analysis for COT conversion and benzene formation Monomer 1 was weighed in a 4-mL sized screw-cap vial with septum and purged with argon. A degassed anhydrous deuterated solvent was added to the vial. The solution of initiator 2 or 3 was added to the monomer solution at once under vigorous stirring. Within 20 mins, a solution of cyclooctatetraene (COT) and 4,4-dimethylbiphenyl (an internal standard) was made, and a tiny amount of the COT solution (~5  $\mu$ L) was sampled out and diluted with 0.5 mL CD<sub>2</sub>Cl<sub>2</sub> to ascertain the initial ratio between COT and the internal standard by <sup>1</sup>H NMR analysis. After that, the solution was added to the reaction vial, and the vial was tightly sealed by using parafilm and Teflon tape. The mixture was stirred for 4.5-16 h at various temperatures (see Table 1). The reaction was quenched by excess ethyl vinyl ether at 0 °C, and then a tiny amount of the crude mixture (~5  $\mu$ L) was sampled out and diluted with 0.5 mL CD<sub>2</sub>Cl<sub>2</sub> to know the final ratio between COT and the internal standard.

COT conversion was calculated from the final COT/(internal standard) ratio divided by initial COT/(internal standard) ratio. Also, benzene formation (%) was calculated from the number of double bonds to form benzene divided by the number of total double bonds theoretically attached to the polymer. (Chemical shift – 4,4-dimethylbiphenyl :  $\delta$  2,37,  $\delta$  7.22,  $\delta$  7.46, CH of COT :  $\delta$  5.76, CH of Benzene :  $\delta$  7.36)

#### How to Calculate the DP<sub>COT</sub> (See Table 1)



In Situ <sup>1</sup>H NMR Analysis for ROMP of COT Monomer 1 was weighed in a screw-cap NMR tube with septum and purged with argon. A degassed anhydrous  $CD_2Cl_2$  was added to the tube. The solution of initiator 2 or 3 was added to the monomer solution at once, followed by vigorous shaking twice. Within 20 mins, a solution of cyclooctatetraene (COT) and 4,4-dimethylbiphenyl (an internal standard) was made, and a tiny amount of the COT solution (~5  $\mu$ L) was sampled out and diluted with 0.5 mL  $CD_2Cl_2$  to ascertain the initial ratio between COT and the internal standard by <sup>1</sup>H NMR analysis. After that, the solution was added to the reaction tube, vigorously shaken once. The tube was tightly sealed by using parafilm and Teflon tape. Then, the reaction was in situ monitored by <sup>1</sup>H NMR. (Feeding ratio was [Norbornene]:[2 or **3**]:[COT] = 50:1:50 and reaction concentration was [COT] = 300 mM)

**Transmission Electron Microscopy (TEM)** The samples for TEM were prepared by dropcasting 10  $\mu$ L aliquot of the polymer solution (0.005 mg polymer/mL CHCl<sub>3</sub>) onto a carbon coated copper grid which was placed on a piece of paper to get rid of excess solvent. The polymer solution was filtered by 0.45- $\mu$ m PTFE filter before drop-casting. This polymer thin film was dried in vacuo for 2 h. The images were obtained on JEM-2100 operating at 200 kV accelerating voltage, using the images acquired with a ORIUS-SC 600 CCD camera (Gatan, Inc.)

Atomic Force Microscopy (AFM) The atomic force microscopy experiments were performed with a thin film prepared by spin-coating one drop of the polymer solution (~0.05mg polymer/mL, CHCl<sub>3</sub>, DCM, Benzene: spinning rate = 3000 rpm for 30 sec, THF: 4000 rpm for 30 sec, Chlorobenzene, toluene: 3000 rpm, 60 sec). All solution were filtered by 0.45- $\mu$ m PTFE filter. The thin films were prepared on both mica and highly ordered pyrolytic graphite (HOPG) substrates. Also, various solvents were used to produce the polymer solution such as DCM, THF, chloroform, chlorobenzene, toluene and benzene. All images were obtained on tapping mode using non-contact mode tips from Nanoworld (Pointprobe® tip, NCHR type) with spring constant of 42 N m-1 and tip radius of ≤8 nm.

**Dynamic Laser Light Scattering (DLS)** The DLS experiments were performed with polymer-chloroform solution (0.1 mg polymer/mL CHCl<sub>3</sub> and 1.0 mg polymer/mL CHCl<sub>3</sub>) in a

quartz glass cell (Hellma Analytics). The size distribution was highly consistent regardless of the solution concentration (0.01-5.0 mg/mL).

In Situ DLS analysis (Fig. S6) Monomer 1 was weighed in a 4-mL screw-cap vial with septum and purged with argon. A degassed anhydrous  $CH_2Cl_2$  was added to the vial. The solution of initiator **3** was added to the monomer solution at once under vigorous stirring. Within 20 mins, cyclooctatetraene (COT) was added. After 15 mins, 3 hours, and 5 hours, a small portion of the reaction solution (~10 µL) was ejected (without quenching), followed by dilution with 1 mL  $CH_2Cl_2$ . Then, the size of the nanoparticles in the solution was monitored by DLS. (Feeding ratio was [Norbornene]:[**2** or **3**]:[COT] = 50:1:50 and reaction concentration was [COT] = 300 mM)

**UV/vis spectroscopy** The UV/vis spectra were obtained from polymer-chloroform solution (0.01-0.1 mg polymer/mL CHCl<sub>3</sub>) in a quartz glass cell (Hellma Analytics).

**Size Exclusion Chromatography (SEC)** Flow rate was 0.8 mL/min and temperature of column was maintained at 35 °C. Samples in 0.5-1.0 mg/mL CHCl<sub>3</sub> were filtered by 0.45-μm PTFE filter before injection.

## 2. Supporting Tables and Figures



Table S1. Elemental analysis of the PA diblock copolymer with narrow *D* (Table 2, entry 3).



**Fig. S1.** NMR spectra of polynorbornene (PN) and PA diblock copolymers synthesised at various reaction temperatures. Identical spectra indicate that not only diblock copolymers spontaneously form supramolecules but also PN blocks remain untouched during the ROMP of COT, which means that the chain-transfer reaction from a PA block to a PN block is highly unlikely.



Fig. S2. IR spectra for PA diblock copolymers synthesised at various temperatures.<sup>S3</sup>



**Fig. S3.** A) CHCl<sub>3</sub> SEC traces monitored by <u>UV/Vis detector</u> at 500 nm. The minor peaks of SEC traces correspond to the disassembled single chains of diblock copolymer with short PA block, not terminated homopolymer of **1** (polynorbornene), because: i) the SEC trace was shifted to higher molecular weight compared to the homopolymer and ii) the homopolymer was totally transparent at 500 nm wavelength, a definitive proof for the presence of the PA second block (See Supporting Information of ref. S4).

The minor trace for one prepared at 0 °C shows a unimodal trace, while others shows broad or even bimodal traces. The major peaks correspond to the supramolecular adducts of PA diblock copolymers.

B) DLS traces of  $PN_{50}$ -b- $PA_{40}$  synthesised at various temperatures. The major peaks of SEC traces indicate that the hydrodynamic volume of supramolecules containing *trans*-major PA core (55 °C) is larger than that of supramolecules containing *cis*-major PA core (0 °C). This is supported by the fact that DLS traces show the average  $D_h$  of supramolecules containing *trans*-major PA core (55 °C) is larger than that of supramolecules containing *cis*-major PA core (0 °C). This is because PA core (55 °C) is larger than that of supramolecules containing *cis*-major PA core (0 °C). This is because PA core with the *trans*-isomer is larger than that with the *cis*-isomer.



**Fig. S4.** UV/vis spectra in chloroform and CP/MAS <sup>13</sup>C solid-state NMR spectra (inset) for PA diblock copolymers synthesised at 0 °C.



**Fig. S5.** (a) In situ DLS intensity profiles during PA diblock copolymerisation at room temperature without quenching or purification (b) DLS intensity profile of the diblock copolymer after purification. (See Experimental Details for the reaction condition)

Average diameter of name	nosphere (D) = 31.895 nm	ı	
$L_n = \frac{\sum_{i=1}^n N_i X_i D}{\sum_{i=1}^n N_i}$	$L_{W} = \frac{\sum_{i=1}^{n} N_i (X_i D)^2}{\sum_{i=1}^{n} N_i X_i D}$	$\left(\frac{\sigma}{L_n}\right) =$	$\sqrt{\frac{L_w}{L_n}-1}$
Statistic analysis for na	anostructures synthesis	ed at 0 °C (F	igure 4a)
Statistic analysis for na # of nanospheres in one nanocaterpillar (X)	nostructures synthesis Frequency (N)	ed at 0 °C (F xN	igure 4a) x²N
Statistic analysis for na # of nanospheres in one nanocaterpillar (X) 1	nostructures synthesis Frequency (N) 0	ed at 0 °C (F XN 0	igure 4a) <u>X²N</u> 0
Statistic analysis for na # of nanospheres in one nanocaterpillar (X) 1 2	nostructures synthesis Frequency (N) 0 8	ed at 0 °C (F <u>xn</u> 0 16	igure 4a) <u>x²N</u> 0 32

	154.4	180.6	1.170	0.411		
	L <sub>n</sub>	L <sub>w</sub>	L <sub>w</sub> /L <sub>n</sub>	σ/L <sub>n</sub>		
Iotai		/6	506		2084	
11		1	11		121	
10		1	10		100	
9		3	27		243	
8		3	24		192	
7		5	35		245	
6		11	66		396	
5		15	75		375	
4		17	68		272	
					200	

Statistic analysis for nanostructures synthesised at r.t. (Figure 4b)

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# of nanospheres in one nanocaterpillar (X)	e Frequency (N)		eres in one pillar (X) Frequency (N) XN		X <sup>2</sup> N	
1		8		8		
2		22	44		88	
3		13	39		117	
4		7		28		
5		9		45		
6		4		24		
7		0		0		
8		1		8		
9		0		0		
10		1 10		100		
Total		65	206		858	
Γ	Ln	Lw	L <sub>w</sub> /L <sub>n</sub>	σ/L <sub>n</sub>	1	
	101.1	132.8	1,315	0.561	1	

**Fig. S6.** Detailed statistic calculation of the nanocaterpillars from the PA diblock copolymer with *narrow* D (Fig. 4a) and that with *broad* D (Fig. 4b). For similar statistical analyses of polymers, see ref. S4.



**Fig. S7.** (a) AFM image of the well-defined nanocaterpillars from the diblock copolymer containing *trans*-PA block with *narrow* D. The inset table shows the average length of nanocaterpillars and their distribution. (b) AFM height profiles of nanocaterpillars before and after *cis/trans* isomerisation. (c) Using AFM profiling analysis, average heights of the nanocaterpillars formed by PN<sub>50</sub>-*b*-PA<sub>200</sub>s were measured before and after *cis/trans* isomerisation.



**Fig. S8.** (a) AFM height profiles at the divarication point of nanocaterpillars. (b) AFM height profile. The height of the divaricators is generally higher than that of other sites.

AFM images of the nanocaterpillars from (c) the PA diblock copolymers with narrower D prepared at 0 °C(with shorter PA block than Fig. 4, DP<sub>COT</sub>=30), (d) the same diblock copolymers after isomerisation, (e) DLS intensity profiles for PN<sub>50</sub>-b- PCOT<sub>30</sub>)

### 3. References

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