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Supporting Information for

One-Pot Synthesis of Polysulfane-Bearing Block Copolymer Nanoparticles with Tunable Size and Refractive Index

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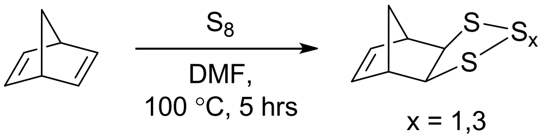
1. Materials and Methods

All air- and moisture-sensitive procedures were conducted under nitrogen atmosphere using standard Schlenk techniques. NMR spectra were obtained from Bruker Ascend TM-400 MHz spectrometer, and all proton chemical shifts were referenced to residual proton resonance of $CDCl_3$ (7.26 ppm). UV-Vis absorption spectra were obtained with PerkinElmer Lambda 35 after correcting for background with a solvent-filled cuvette. Typical concentration of polymer nanoparticles for UV-Vis measurements was 0.1 mg/mL. Dynamic light scattering (DLS) for nanoparticle size and size distribution measurements were conducted on Malvern Zetasizer Nano ZS90 using intensity-based distribution. Transmission electron microscopy (TEM) images were obtained on Carl Zeiss LIBRA 120 microscope using 120 kV acceleration voltage. Samples were cast onto carbon-coated copper grids from chloroform solutions (0.05 mg/mL) for size control studies and from chlorobenzene solutions (0.05 mg/mL) for heating experiments. Scanning electron microscopy (SEM) images were obtained from JEOL JSM-6701F microscope. Average diameter of polymer nanoparticles and standard deviations were calculated by averaging 30 particles from TEM or SEM images using ImageJ software (developed at the National Institute of Health). Elemental analysis was conducted on Thermo Scientific Flash 2000 CHNS/O Analyzer. X-ray photoelectron spectroscopy (XPS) was carried out on Kratos AXIS-HSi at the Research Institute of Advanced Materials (RIAM) at Seoul National University. Ellipsometry was done using Gaertner Scientific Corporation Stokes Waferskan Ellipsometer L2W15S830 at two fixed wavelengths (632.8 nm HeNe gas laser and 830.0 nm laser diode). High-resolution mass spectrometry (HRMS) was obtained at the Seoul National University National Center Inter-University Research Facilities using EI ionization technique. Thermogravimetric analyses were conducted on Waters TGA Q500 with a heating rate of 10 °C/min. Alpha-step measurements were conducted on KLA Tencor Alpha-Step IQ. Analytical thin-layer chromatography (TLC) was performed using Merck Kieselgel 60F-254 plates, and column chromatography was carried out using Merck silica gel 60 (70~230 mesh). Spectral grade solvents were used unless otherwise noted. Dichloromethane was distilled over calcium hydride and degassed by bubbling argon through directly prior to use. Tetrahydrofuran was distilled over sodium/benzophenone and degassed by bubbling argon through directly prior to use. Monomer *N*-cyclohexyl-*exo*-norbornene-5,6-dicarboximide[1] (ChNDI) was prepared according to literature procedures. Grubbs third-generation catalyst used in this study was prepared according to previous reports, using unsubstituted pyridine.[2] All other commercially available chemicals were used as received.

2. Experimental Procedures



Cyclic Polysulfane Monomer (CPM, 1). A mixture of elemental sulfur (5.0 g, 160 mmol S_8) and anhydrous, degassed dimethylformamide (50 mL) under argon was heated to 100 °C. Norbornadiene (4.0 mL, 39 mmol), passed through a plug of basic alumina directly prior to use, was then added. After stirring further at 100 °C for 5 hours, the reaction was poured into deionized water (600 mL) and subsequently extracted with diethyl ether. The ethereal layer was washed once with water, dried over magnesium sulfate, and concentrated *in vacuo*. The resulting dark brown oil was subjected to column chromatography (silica gel, 9:1 hexanes/DCM) to give a mixture of pentathiepane, tritholane, and episulfide derivatives. The product mixture was further subjected to vacuum (50 mTorr) for 24 hours to afford exclusively the pentathiepane (x = 3) and triothiolane (x = 1) derivatives in 1:3.5 molar ratio (as determined through ^{1}H NMR, according to proton resonance assignments provided in literature,[3] see below) as a pale yellow oil (408 mg, 5.2 %). HRMS (EI): calcd. (x = 1) 187.9788, found 187.9788. calcd. (x = 3) 251.9230, found 251.9229.

General procedure for the synthesis of pChNDI$_{100}$-*b*-pCPM$_m$. *N*-cyclohexyl-*exo*-norbornene-5,6-dicarboxmide (ChNDI, 80.0 mg, 0.326 mmol) in 0.5 mL solvent (DCM or THF) and the pyridine-bearing 3rd generation Grubbs catalyst (2.37 mg, 0.00326 mmol) in 0.5 mL solvent were prepared in separate oven-dried vials under argon atmosphere. ChNDI solution was then transferred to the catalyst solution under stirring. After stirring at room temperature for 20 minutes, a desired amount of CPM in solvent (DCM or THF) was added so that the final concentration of CPM in the polymerization mixture was 0.49 M. The reaction was stirred for an additional 5 hours followed by an addition of excess ethyl vinyl ether. After stirring in the presence of ethyl vinyl ether for 20 minutes, the reaction was carefully poured into vigorously stirred methanol and the BCP was obtained as an off-white precipitate. The polymer was further purified by iterative dissolution/reprecipitation using DCM and methanol followed by drying under vacuum at room temperature (Yield: 51~62 %). ^{1}H NMR (300 MHz, CDCl$_3$) for pChNDI$_{100}$-*b*-pCPM$_{40}$: δ 5.74 (1H), 5.40-5.60 (1H), 3.86 (1H), 3.33 (1H), 2.60-3.15 (3H), 2.10 (3H), 1.79 (2H), 1.48-1.68 (4H), 1.1-1.35 (3H). Homopolymer, pChNDI, has identical ^{1}H NMR spectrum. Anal. Calcd for pChNDI$_{100}$-*b*-pCPM$_{20}$: C, 68.10; H, 7.17; N 4.76; S, 8.44. Found: C, 68.04; H, 7.17; N, 4.65; S. 7.12. Anal. Calcd for pChNDI$_{100}$-*b*-pCPM$_{40}$: C, 64.79; H, 6.76; N 4.08; S, 15.05. Found: C, 66.18; H, 6.83; N, 4.33; S. 12.98.

General procedure for the synthesis of pChNDI$_{50}$-*b*-pCPM$_m$ for nanoparticle size control studies. Reactions were carried out using the general conditions for pChNDI$_{100}$-*b*-pCPM$_m$ shown above. Detailed reaction conditions and the corresponding nanoparticle size as determined from DLS studies is summarized below.

Table S1. Reaction conditions for the preparation of pChNDI$_{50}$-*b*-pCPM$_m$ BCP for size control studies.

Feed Ratio (M/I)		Solvent	Concentration (M)		Reaction Time		Conversion[a]		Real DP	DLS (nm, CHCl$_3$)
ChNDI	CPM		1st block	2nd block	1st block	2nd block	1st block	2nd block		
50	25	DCM	0.4	0.1	10min	1h	Full	Full	50:25	28.62
50	50	DCM	0.3	0.2	15min	5h	Full	97%	50:48	36.35
50	100	DCM	0.3	0.3	15min	12h	Full	75%	50:75	44.83
50	100	DCM	0.3	0.35	15min	5h	Full	86%	50:86	46.97
50	100	THF	0.5	0.5	20min	4h40min	95%	98%	48:98	49.62

[a] Determined through the ratio of integrals of polymer olefin resonance and monomer olefin resonance in ^{1}H NMR spectrum.

Preparation of BCP Thin Films for SEM, Ellipsometry, and Thin-Film UV-Vis Measurements. BCP nanoparticles for SEM imaging were prepared by drop-casting 0.05 mg/mL solution of polymer in chloroform onto piranha-cleaned silicon wafer. Polymer thin films (thickness ~150 nm) for ellipsometry were prepared by spin-casting a 20 mg/mL solution of polymer in chloroform onto piranha-cleaned silicon wafer at 4000 rpm for 30 seconds followed by drying under vacuum overnight. The refractive index of pChNDI homopolymer film prepared in this manner was identical to the value reported in literature.[4] To prepare thicker, free-standing films (average thickness ~10 μm), a 25 mg/mL solution of polymer in chloroform was drop-cast onto a slide glass substrate.

3. Figures

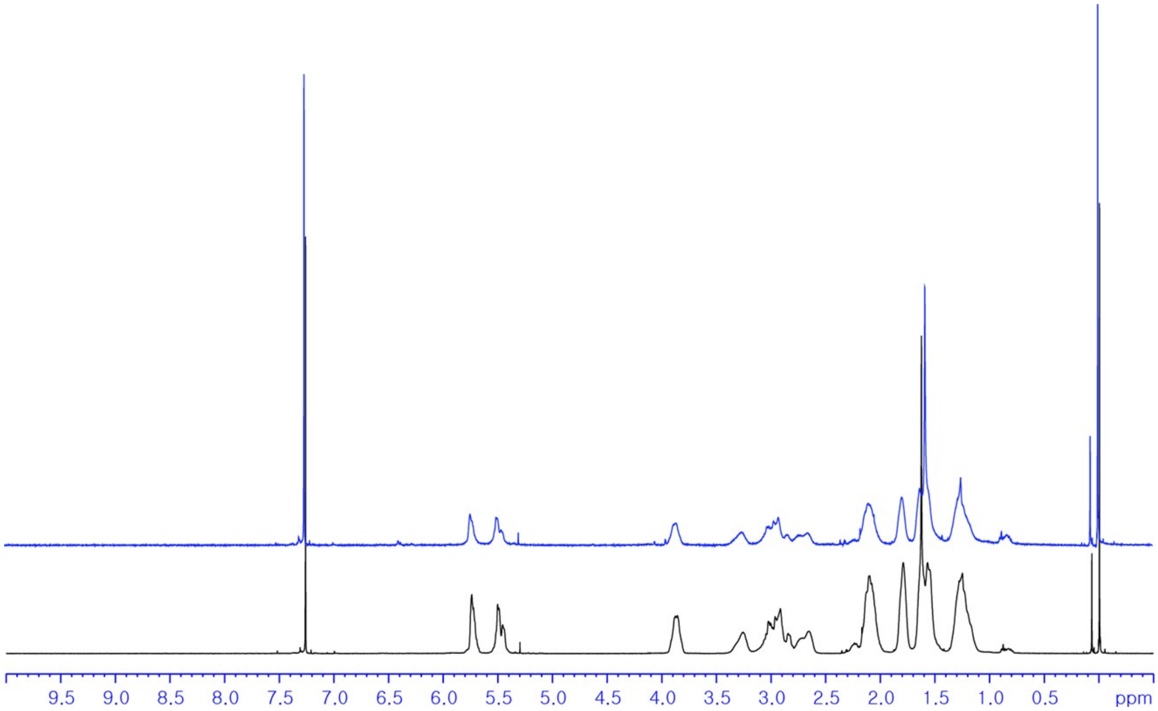


Figure S1. ^{1}H NMR spectra ($CDCl_3$) of pChNDI homopolymer (black) and pChNDI$_{50}$-*b*-pCPM$_{100}$ BCP (blue).

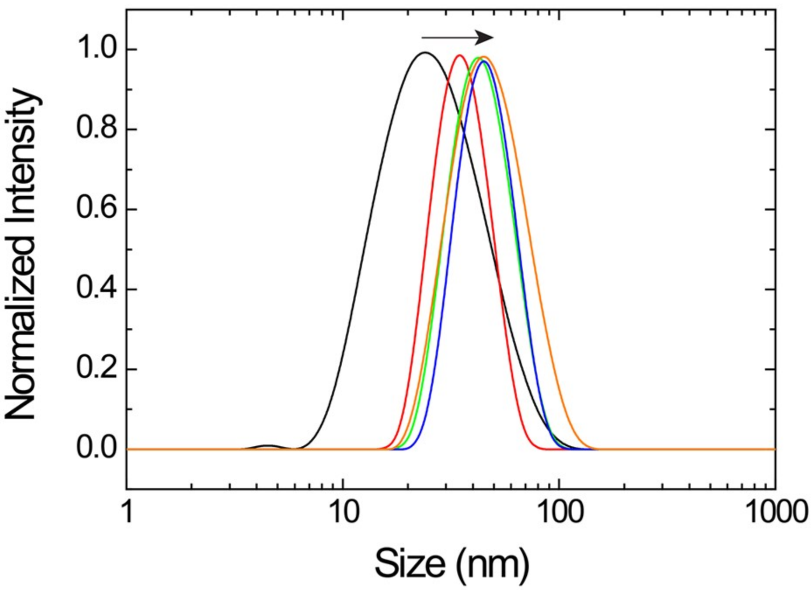


Figure S2. DLS traces of pChNDI$_{50}$-*b*-pCPM$_{m}$ in solution (1 mg/mL in chloroform) with m = 25 (black), 48 (red), 75 (green), 86 (blue), and 98 (orange).

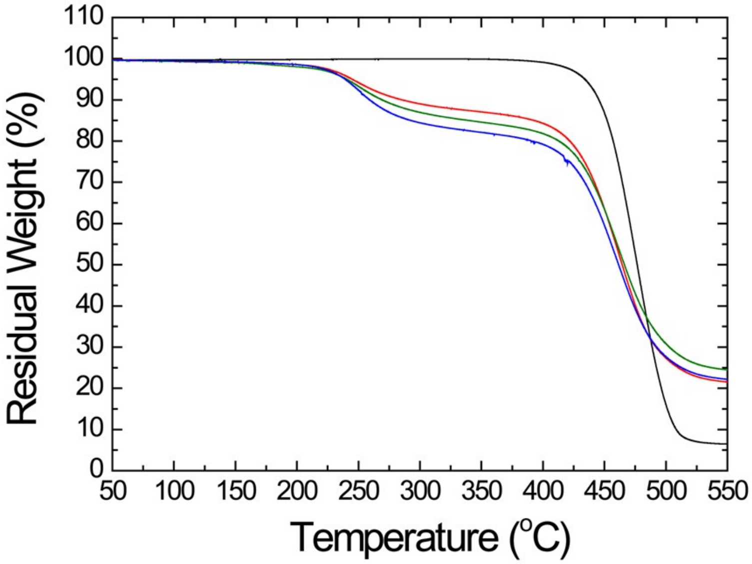


Figure S3. TGA traces of pChNDI homopolymer (black), pChNDI$_{100}$-*b*-pCPM$_m$ BCP with m = 30 (red), 48 (green), and 60 (blue).

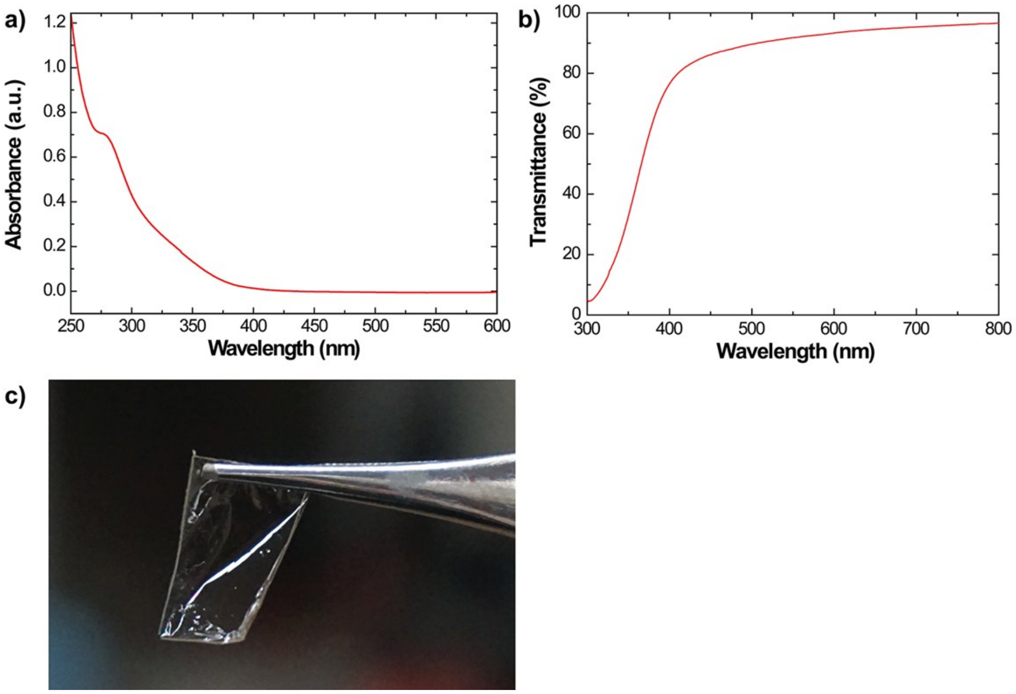
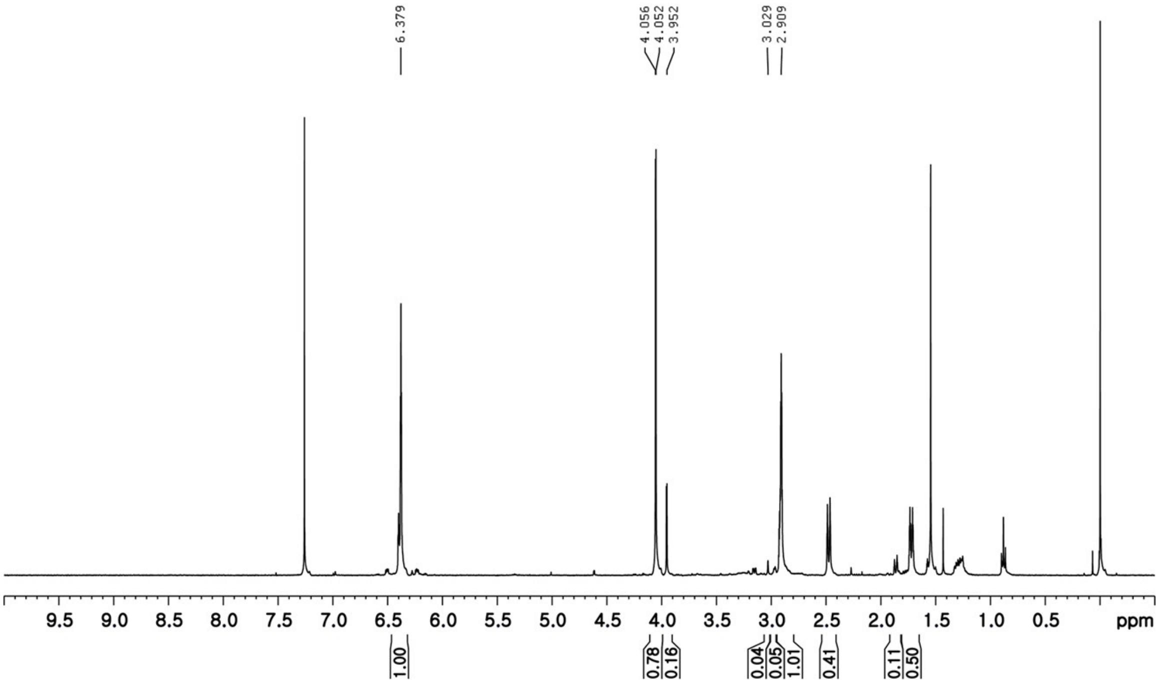
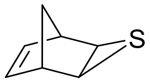


Figure S4. (a) UV-Vis absorption spectrum of pChNDI$_{100}$-*b*-pCPM$_{40}$ in chloroform (absorptivity at 285 nm = 0.05), (b) transmittance *versus* wavelength of pChNDI$_{100}$-*b*-pCPM$_{40}$ film (~ 10 μm average thickness, determined using an alpha-step profilometer) on microscope slide glass prepared by drop casting, and (c) a photograph of the drop-cast film after peeling off from the substrate.

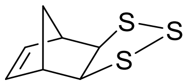
4. ^{1}H NMR Spectrum of CPM (1)



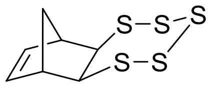
From the above ^{1}H NMR spectrum, molar ratio of various cyclic polysulfane-bearing norbornene derivatives was determined according to peak assignments provided in the literature[3] as summarized below.



^{1}H NMR ($CDCl_3$) for the episulfide: δ 6.36 (m, 2H), 3.00 (d, 2H), 2.95 (s, 2H), 1.84 (d, 1H), 1.28 (d, 1H)



^{1}H NMR ($CDCl_3$) for the trithiolane: δ 6.40 (m, 2H), 4.05 (d, 2H), 2.90 (s, 2H), 2.50 (d, 1H), 1.73 (d, 1H)



^{1}H NMR ($CDCl_3$) for the pentathiepane: δ 6.40 (m, 2H), 3.95 (d, 2H), 2.90 (m, 2H), 1.86 (d, 1H), 1.56 (d, 1H)

4. Reference

(1) Contreras, A. P.; Tlenkopatchev, M. A.; Lopez-Gonzalez, M. D.; Riande, E. *Macromolecules* **2002,** *35* (12), 4677.

(2) Kang, E.-H.; Lee, I.S.; Choi, T.-L. *J. Am. Chem. Soc.* **2011**, *133*, 11904.

(3) Bartlett, P. D.; Ghosh, T. *J. Org. Chem.* **1987,** *52* (22), 4937.

(4) Spring, A.M.; Yu, F.; Qiu, F.; Yamamoto, K.; Yokoyama, S. *Polym, J.* **2014**, *46*, 576.