

Supplemental Information

Controlled folding of a novel electroactive polyolefin via multiple sequential orthogonal intra-chain interactions.

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Experimental Section

General Methods. Size exclusion chromatography (SEC) was performed on a Tosoh EcoSEC dual detection (RI and UV) GPC system coupled to an external Wyatt Technologies miniDAWN Treos multi angle light scattering (MALS) detector and a Wyatt Technologies ViscoStarII differential viscometer. Samples were run in THF at 40 °C at a flow rate of 0.35 mL/min. The column set was two Tosoh TSKgel SuperMultipore HZ-M columns (4.6x150 mm), one Tosoh TSKgel SuperH3000 column (6x150mm) and one Tosoh TSKgel SuperH4000 column (6x150mm). Increment refractive index values (dn/dc) were calculated online assuming 100% mass recovery (RI as the concentration detector) using the Astra 6 software package (Wyatt Technologies) by selecting the entire analyte peak. Absolute molecular weights and molecular weight distributions were calculated using the Astra 6 software package. This method gave the expected values for polystyrene ($dn/dc = .185$, $M_n = 30k$) when applied to a narrow PDI PS standard supplied by Wyatt. Relative molecular weights were obtained vs. polystyrene standards (PStQuick MP-M, Tosoh) and calculated using the EcoSEC software package (Tosoh). 1H NMR (400 MHz) spectra were recorded on a Varian Associates Mercury 400 spectrometer. Solvents ($CDCl_3$ or d_8 -THF) contained 0.03% v/v TMS as an internal reference, chemical shifts (δ) are reported in ppm relative to TMS. Peak abbreviations are used as follows: s=singlet, d=doublet, t=triplet, m=multiplet, br=broad. Mass spectroscopy (MS) was performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). Fourier-transform infrared spectra (FTIR) measurements were recorded on a BRUKER VECTOR 22 Spectrometer by averaging 128 scans at a resolution of 4 cm^{-1} in the range of $4000\text{-}400\text{ cm}^{-1}$. Cyclic voltametry (CV) was investigated on a CHI 660A

Electrochemical Workstation (CH Instruments, USA) with a conventional three-electrode cell, using a Ag/AgCl as the reference electrode, a platinum wire electrode as the counter electrode, and a glassy carbon electrode (GCE, Φ 3.0 mm) as the working electrode. Spectroelectrochemical measurements were carried out in a cell built from a 1 cm commercial cuvette using a UV-2501 PC Spectrometer (SHIMADZU). The ITO-coated glass was used as the working electrode, a Pt wire as the counter electrode, an Ag/AgCl cell as the reference electrode and 0.5 mol L⁻¹ H₂SO₄ was used as the electrolyte. UV-vis spectra were performed on UV-2501 PC Spectrometer (SHIMADZU) in dilute DMAc solution. Hydrodynamic radii of single-chain polymer nanoparticles in THF solutions were determined by dynamic light scattering (DLS). The DLS instrumentation consisted of a Malvern Instruments ZEN3600 operating at 25 °C with a 633 nm laser module. Measurements were made at a detection angle of 173° (backscattering) and Zetasizer software (version 6.12) was utilized to analyze the data..

Materials

1,5-cyclooctadine, 2nd generation Grubbs ruthenium catalyst, exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride (exo-ONA), N-phenyl-p-phenylenediamine, p-phenylenediamine, 1,6-Hexanedithiol were purchased from Aldrich. All other reagents were obtained from commercial sources and used as received without further purification. Distilled and deionized water was used. Optically transparent ITO glass substrates (Reintech electronic technologies CO., 10 Ω /square) with dimensions of 6.0×0.6 cm² were used as thin film electrodes.

Synthesis of Aniline Tetramer (AT)

The aniline tetramer in emeraldine state was synthesized by oxidative coupling of *N*-phenyl-*p*-phenylenediamine in the presence of ferric chloride hexahydrate as an oxidant according to the published method.¹

MALDI-TOF-MS: m/z calculated for $C_{24}H_{22}N_4 = 366.5$. Found 366.6. 1H NMR (d_6 -DMSO): $\delta = 7.78$ (s, 1H, due to -NH-), $\delta = 7.68$ (s, 1H, due to -NH-), $\delta = 7.43$ (s, 1H, due to -NH-), $\delta = 7.12$ (t, 2H, due to Ar-H), $\delta = 6.87$ (m, 12H, due to Ar-H), $\delta = 6.65$ (t, 1H, due to Ar-H), $\delta = 6.51$ (d, 2H, due to Ar-H), $\delta = 4.62$ (s, 2H, due to -NH₂).

Synthesis of Poly(norbornene anhydride-*co*-cyclooctadiene) (PNCO)

Ring opening metathesis polymerization (ROMP) reactions were carried out in three-necked round-bottom flask under a dry argon atmosphere using 2nd generation Grubbs ruthenium catalyst. First, 0.648g (6mmol) of 1,5-cyclooctadiene was dissolved in 4 mL THF. Then 0.051 mg (0.06 mmol) of Grubbs catalyst in 2 mL THF was added into the 1,5-cyclooctadiene solution. The reaction was stirred at room temperature under dry argon atmosphere. After 2.5 h stirring, 0.332 g (2 mmol) *exo*-ONA dissolved in 2 mL THF was added into the above polycyclooctadiene solution. The reaction was stirred for another 5 h and then terminated by adding several drops of ether-vinyl ether. 1H NMR (d_6 -DMSO): $\delta = 5.36$ (m, due to -CH=CH- in polybutadiene part), $\delta = 1.93$ -2.07 (m, due to -CH₂- in polybutadiene part), $\delta = 5.75$ and 5.95 (m, due to *cis* and *trans* -CH=CH- in poly(oxanorbornenyl dicarboxylic anhydride) part), $\delta = 4.97$ (m, due to the proton in secondary carbon group), $\delta = 3.68$ (m, due to the proton in tertiary carbon group). GPC-MALS $M_n = 15,000$, PDI = 1.19

General Polymer Modification Procedures

Functionalization with Aniline Tetramer (PNCO-AT)

Different amounts of aniline tetramer (25 mol%, 50 mol%, 75 mol% or 100 mol% relative to the amount of anhydride units present in the polymer backbone) dissolved in 20 mL of THF were added to a solution of the poly(norbornene anhydride-co-cyclooctadiene) copolymer. The reaction was stirred for 10 h under argon. The polymer was then precipitated into 200 mL methanol. The polymer was isolated by filtration and dried under the vacuum at 40°C for 24 h. According to the feed ratio, the polymers are labeled here as PNCO-AT25, PNCO-AT50, PNCO-AT75, and PNCO-AT100. ¹H NMR (d₆-DMSO): δ = 5.36-5.95 (m, due to -CH=CH-), δ = 1.93-2.07 (m, due to -CH₂-), δ = 4.97 and 3.68 (m, due to the proton in aliphatic group), δ = 9.45, 7.78, 7.69 and 7.64 ppm (m, due to the -NH- from oligoaniline), δ = 7.47-6.67 (m, due to Ar-H), δ = 12.75 (m, due to -COOH). See Table S1 for complete molecular weight details.

Intra-chain Covalent Cross-linking by Amidation Reaction (PNCO-AT50-DA)

A solution of p-phenylenediamine in THF was added dropwise to a stirring solution of PNCO-AT50 in THF over 20 min, and then the resulting solution was allowed to stir for another 10 h at the room temperature. The extent of covalent intra-chain interactions was controlled by controlling the amount of diamine added (25 mol%, 50mol%, 75 mol%, or 100 mol%) amine groups based on the amount of remaining unreacted anhydride units in the backbone (denoted with a suffix). The resulting solution was filtered by the 0.45 μm syringe filter prior to SEC characterization. See table S1 for complete molecular weight data.

Intra-chain Covalent Cross-linking by Thiol-ene “click” Reaction (PNCO-AT50-SH) Varying amounts of 1,6-hexanedithiol (10-30 mol% hexanedithiol relative to the total number of cyclooctadiene units within the polymer, denoted with a suffix)) was added into 2 mL of a 1 mg/mL THF solution of PNCO-AT50 in a quartz tube. The mixture was degassed by sparging with argon, then the thiol-ene reaction (without a photoinitiator) was performed under UV light (254 nm) for 2 min without stirring at room temperature (intensity $\sim 0.018 \text{ W/m}^2$). The resulting solution was filtered by the 0.45 μm syringe filter prior to SEC characterization. NMR characterization of this step is precluded by the requisite high dilution. See table S1 for complete molecular weight data.

Polymer ^a	M_n^b (kDa)	M_w^b (kDa)	PDI ^b	$M_n \text{ Th}^c$ (kDa)	R_n^d (nm)
PNCO	15.0	17.8	1.19	16.1	6.5
PNCO-AT25	17.4	20.6	1.18	17.3	6.1
PNCO-AT50	19.9	23.9	1.20	19.7	5.7
PNCO-AT75	22.5	27.0	1.20	22.1	5.3
PNCO-AT100	26.6	31.4	1.18	24.5	4.8
PNCO-AT50-DA25	20.7	25.4	1.23	20.2	5.3
PNCO-AT50-DA50	22.6	26.6	1.18	20.5	4.9
PNCO-AT50-DA75	22.8	27.4	1.19	20.8	4.6
PNCO-AT50-DA100	24.1	29.1	1.21	21.1	4.3
PNCO-AT50-SH10	22.0	25.2	1.15	21.6	5.5
PNCO-AT50-SH20	22.7	26.0	1.15	23.3	4.8
PNCO-AT50-SH30	25.6	31.7	1.23	25.0	4.5
PNCO-AT50-DA50-SH20	23.3	27.6	1.18	23.9	4.3

Table S1: Size Exclusion Chromatography and DLS data. a: numbers in the polymer names refer to the mol % of cross-linker in relation to residual reactive comonomer in the polymer, i.e. PNCO-AT50-DA25 indicates 50% of the anhydride units were reacted with aniline tetramer, 25% of those remaining were reacted with diamine cross-linker. See text and experimental section for details. b: From SEC-MALS c: Calculated based on M_n of PNCO assuming complete reaction of the added cross-linker functional groups. d: from dynamic light scattering.

Information on SEC-MALS characterization.

In a typical SEC experiment molecular weights are obtained by comparing a sample's retention time to that of a polystyrene standard of known molecular weight (i.e. relative molecular weight). This relative molecular weight is therefore correlated to a sample's hydrodynamic volume as chromatographic separation in SEC is based on this volume. In polymer folding studies, changes in hydrodynamic volume are brought about by intrachain coupling interactions, which makes molecular weight determination using standard calibration impossible. For example, in our study we are adding external cross-linkers to the original chain to induce folding, where by we add considerable mass to the chain. Conventional calibration applied here would imply a decrease in molar mass of the chain. Using multi angle light scattering to measure the absolute molecular weight of the sample, a technique that doesn't rely on chromatographic separation and is therefore not coupled to retention time, circumvents this complication. This provides an excellent tool not only for determining the sample molecular weight, but also for confirming that the observed shifts in retention time are truly result of folding due to intrachain interactions.

Fabrication of Electrochromic Electrode by PNCO

The ITO substrates were washed ultrasonically in the acetone for 6 min and in the deionized water for another 6 min, then air dried before use. Polymer (0.02 g) was dissolved in 1 mL DMAc to form a dark solution, and filtered through 0.2- μm poly(tetrafluoroethylene) syringe filter. Then, polymer films were spin-coated onto the ITO substrates by the DMAc solution. The spin-coating process was firstly 500 rpm for 5

s and then 1000 rpm for 30 s. Before electrochromic measurements, a copper tape (1.0 cm × 0.5 cm) was applied to the top edge of ITO substrates as the bus bar.

Supporting Figures

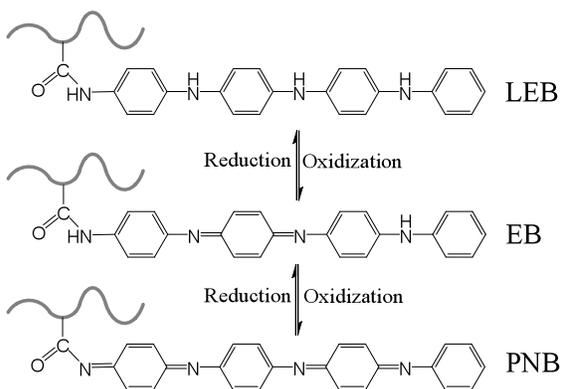
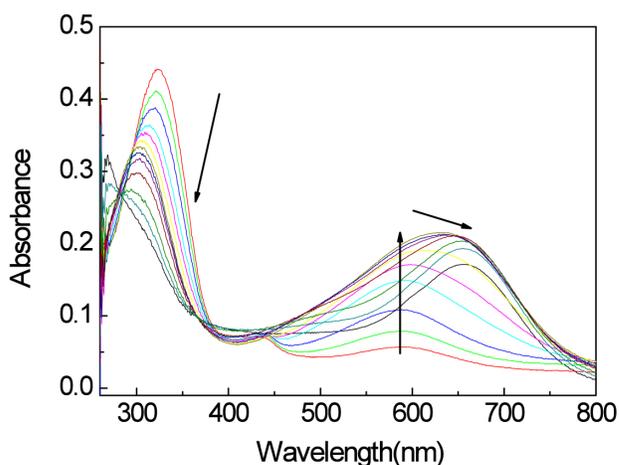


Fig S1: UV-vis spectra monitoring the chemical oxidation of the polymer by the addition of trace amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. From the leucoemeraldine oxidation state to the emeraldine oxidation state; then from the emeraldine oxidation state to the pernigriline oxidation state (structures of each state are shown).

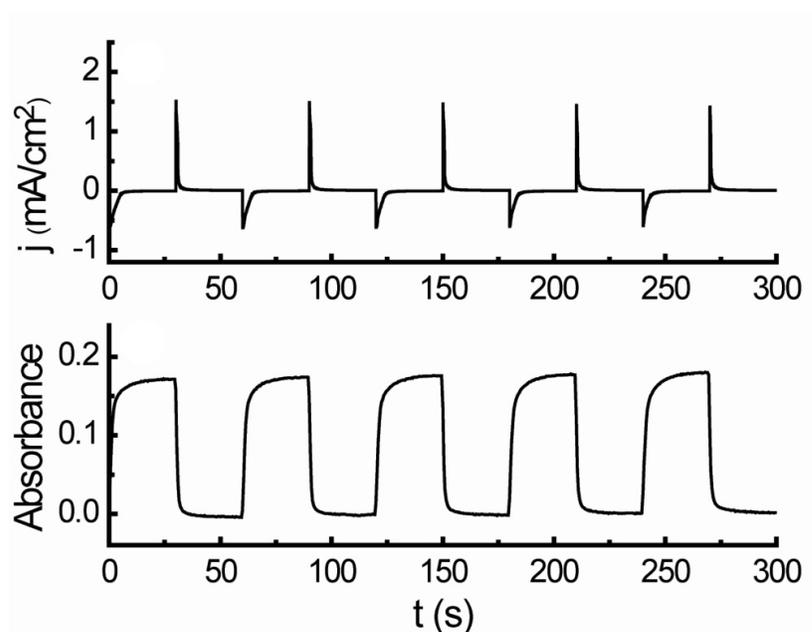


Fig S2: Spectrochronoamperometry for PNCO-AT100. The detection was conducted in the optical contrast at 700 nm during repeated potential stepping between neutral (-0.2 V) and oxidized state at 0.6 V with an interval of 30 s for both potentials. The first 5 cycles are present above. The optical contrast value ($\% \Delta T$) was found to be 30% at 700nm measured between its coloring and bleaching states. The switching time was the time required to bring the polymer to its reduced state from its oxidized state or vice versa. Here, it was defined as the time required for reaching 90% of the full change in coloring/bleaching process. The polymer film required a switching time of 5.0 s at 0.6 V for the coloring process at 700 nm and 1.5 s at -0.2 V for bleaching, which is an acceptable switching rate for a conductive polymer electrochromic devices. Moreover, the coloration efficiency CE ($\eta = \Delta OD/Q$) is a practical tool to measure the power requirements of an electrochromic material. The electrochromic behavior of the polymer exhibited CE up to $91 \text{ cm}^2/\text{C}$ (at 700 nm) at the oxidation stage, which is a higher result as PANI electrochromic devices.

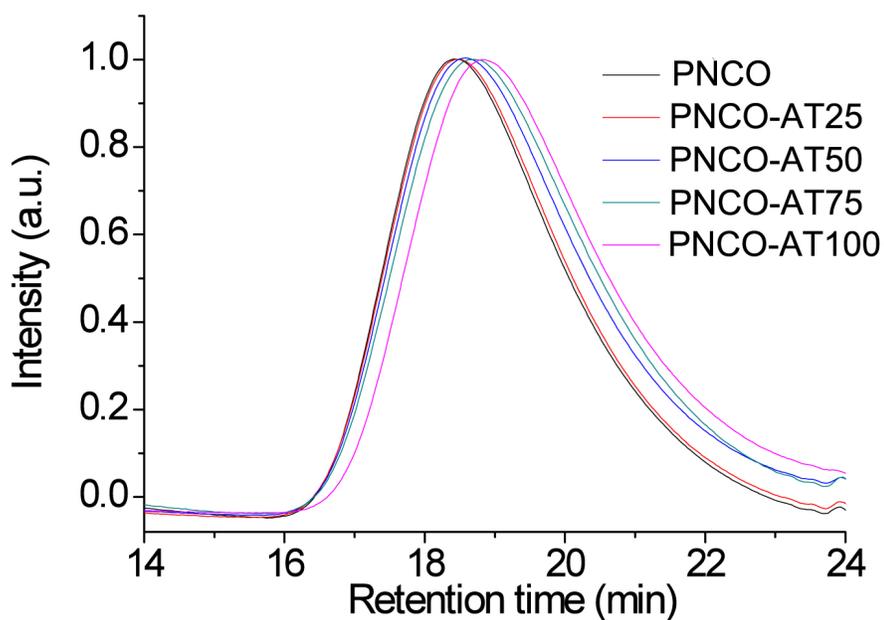


Fig. S3: SEC traces for PNCO before and after functionalization with aniline tetramer.

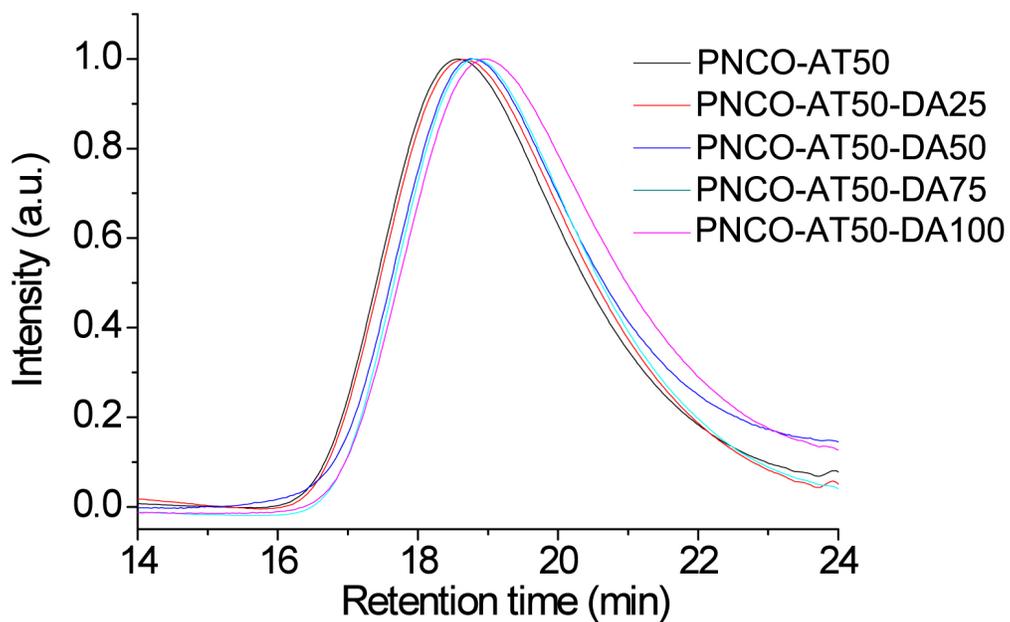


Fig. S4: SEC traces of PNCO-AT50 before and after covalent folding via reaction with diamine.

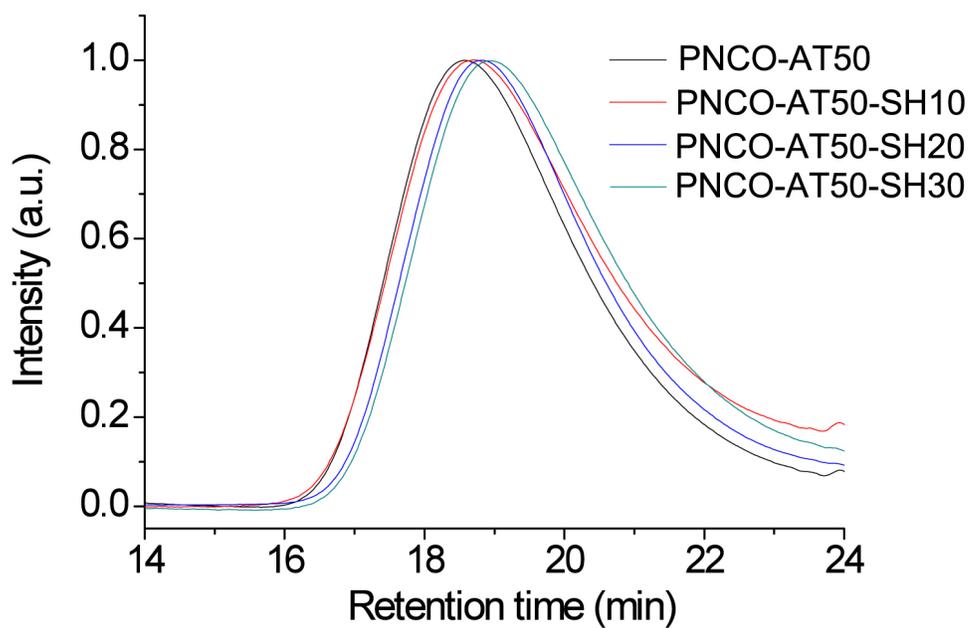
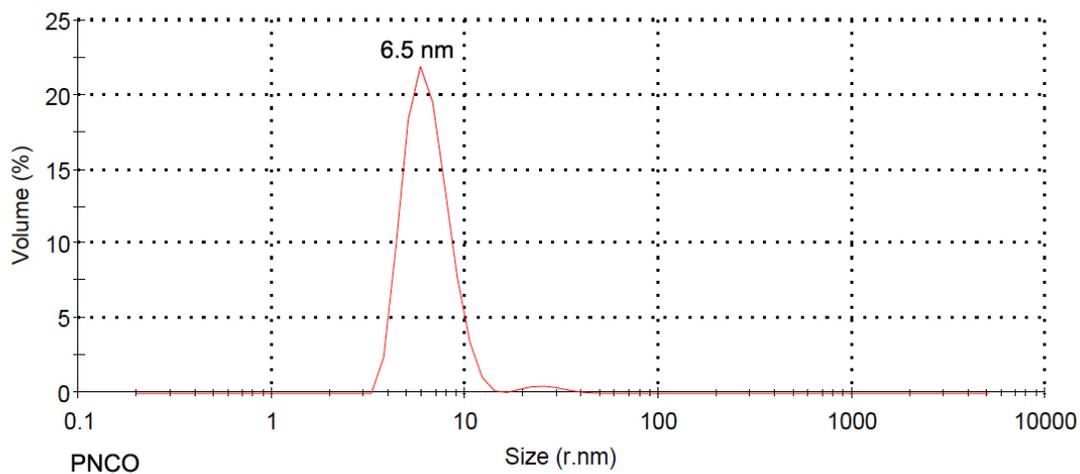
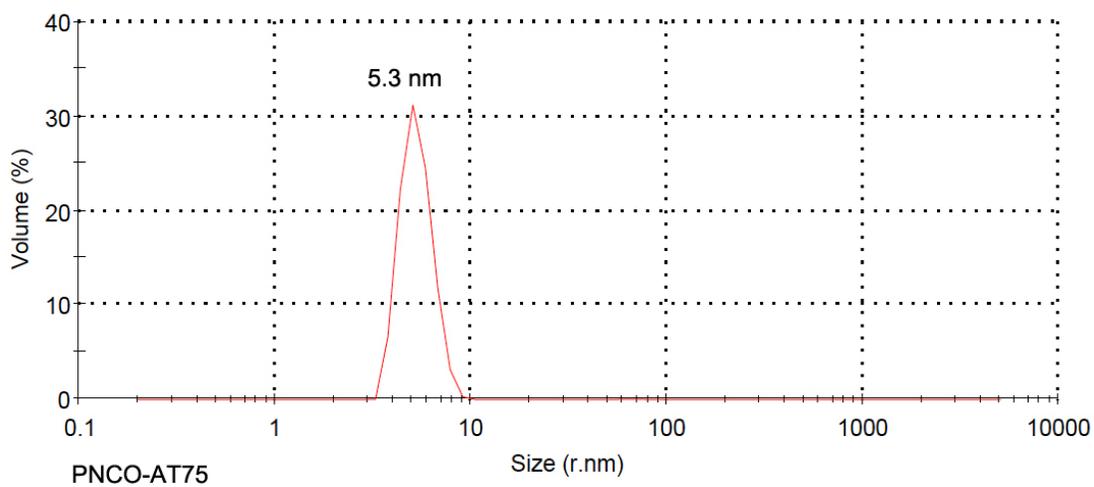
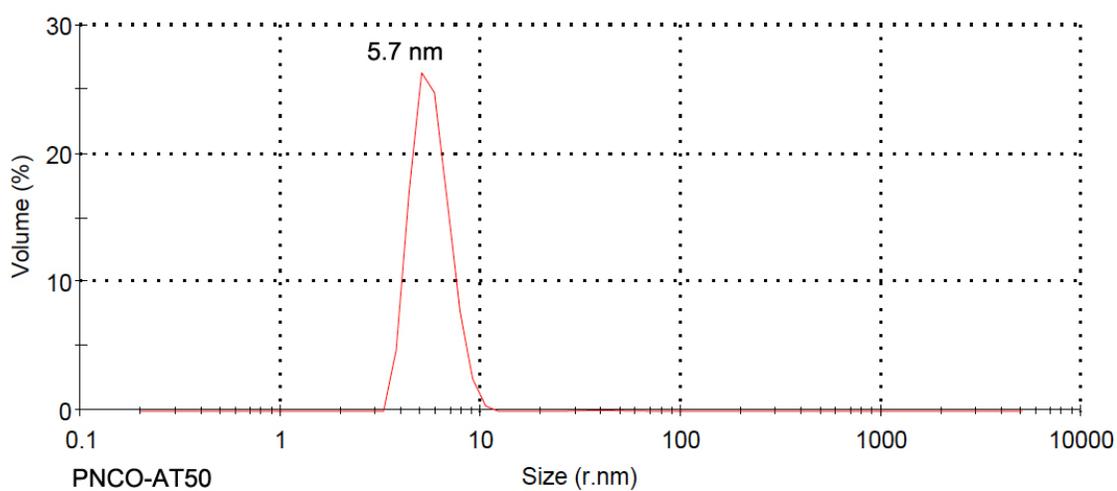
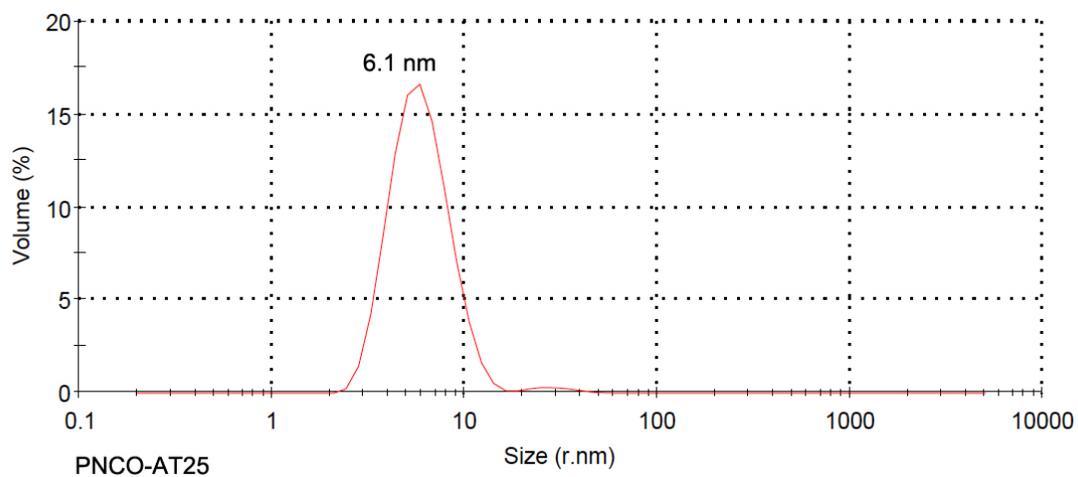
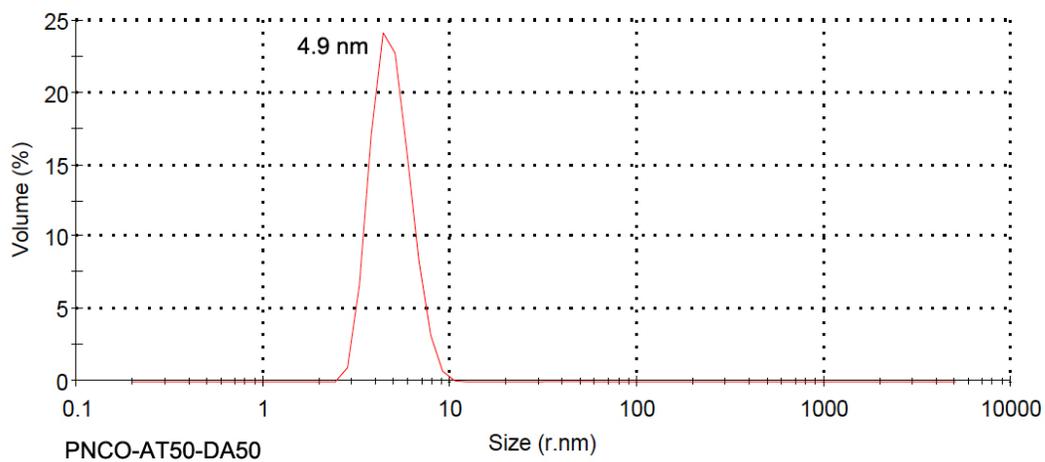
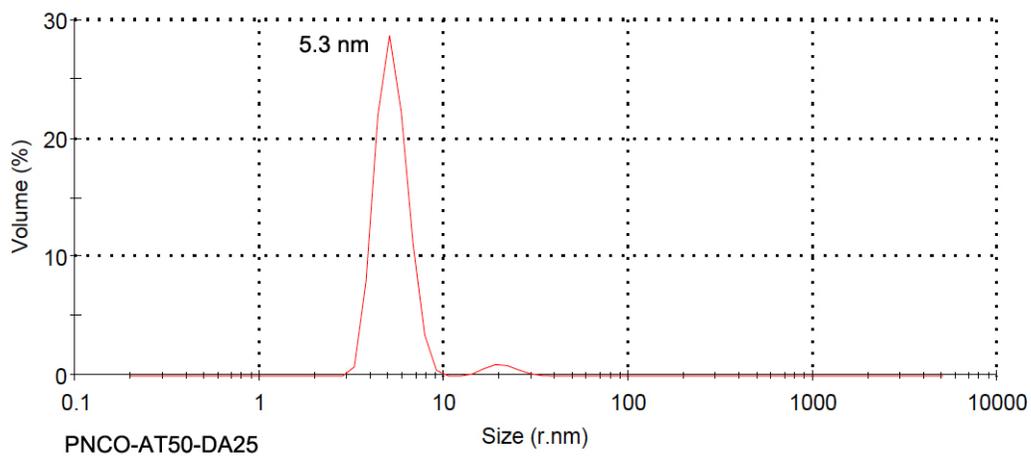
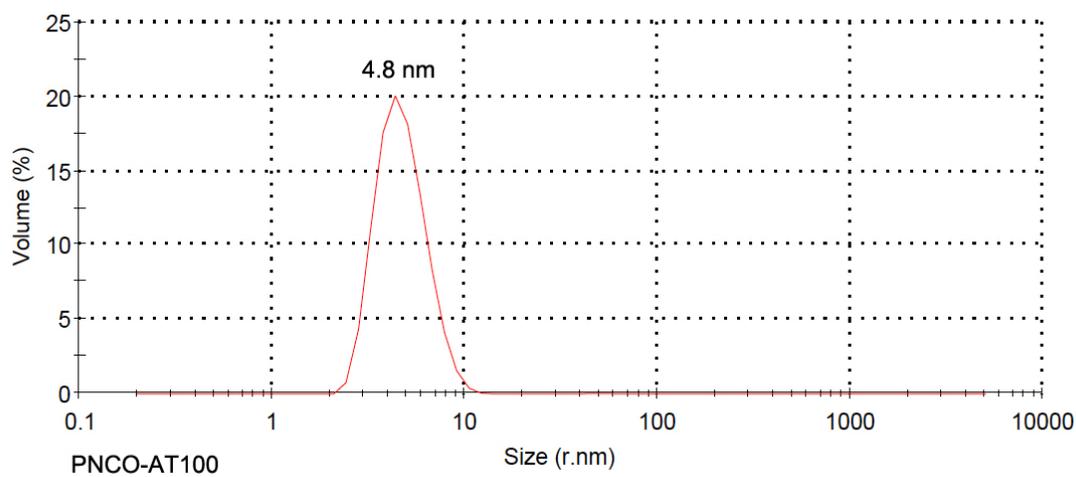


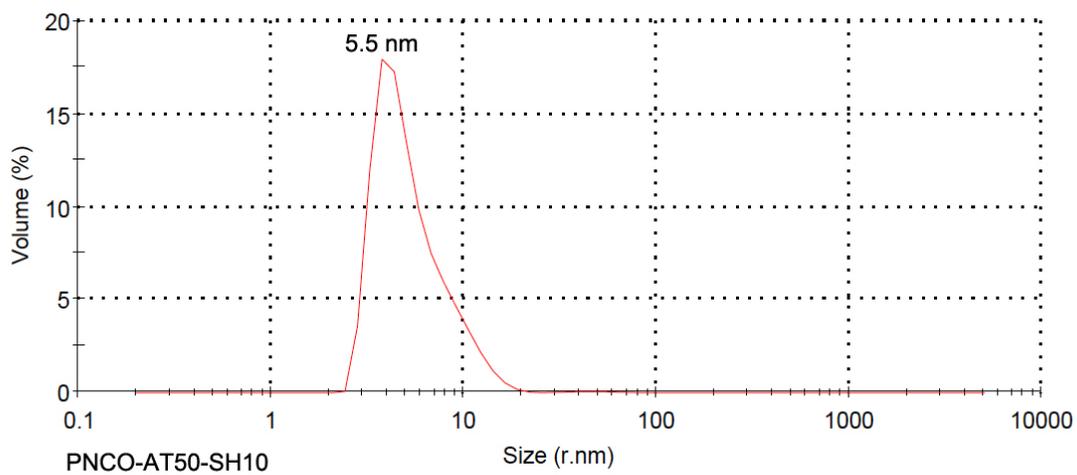
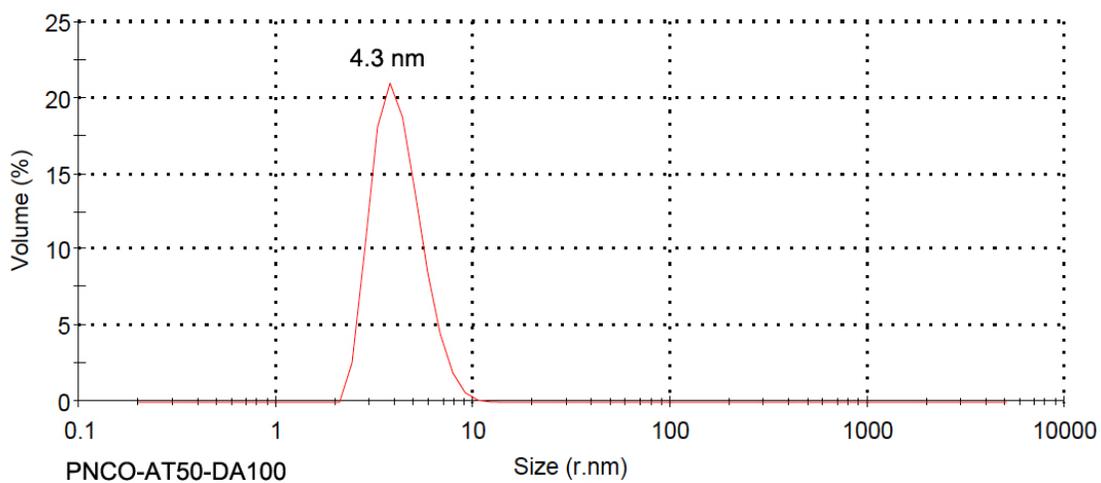
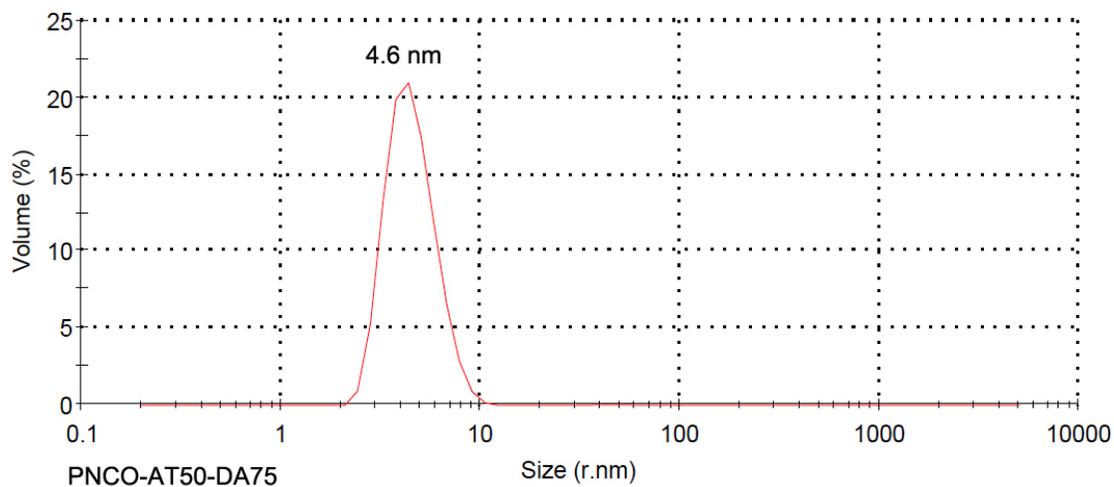
Fig. S5: SEC traces of PNCO-AT50 before and after covalent folding via thiol-ene chemistry.

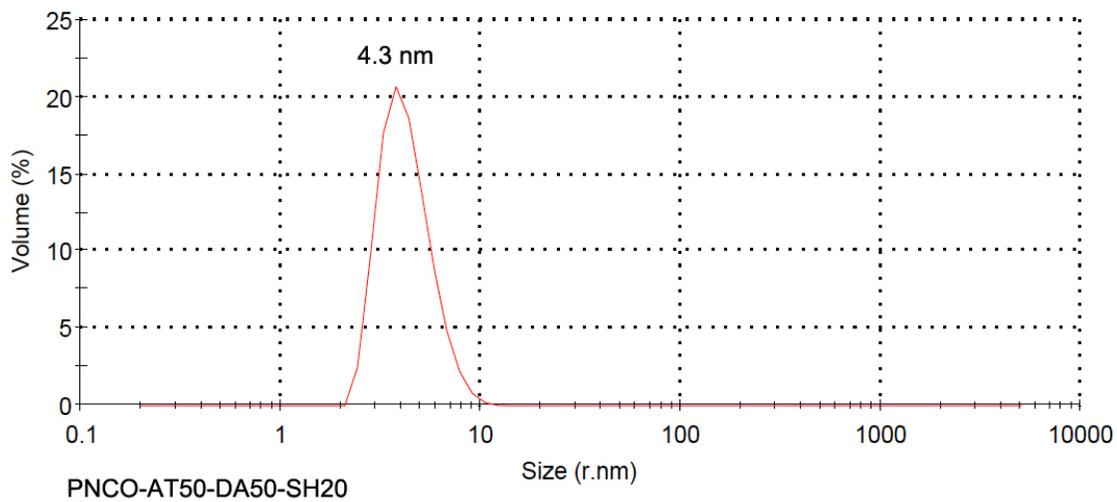
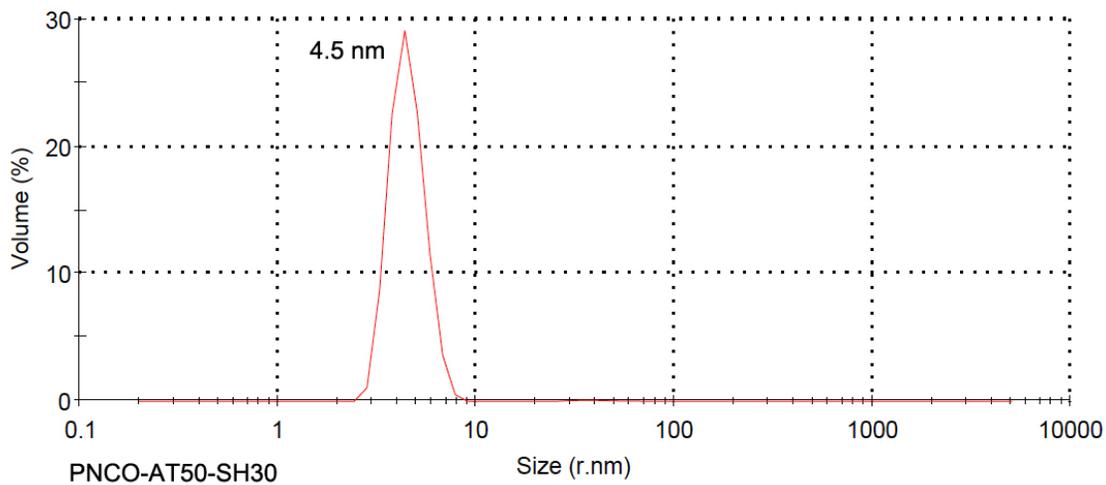
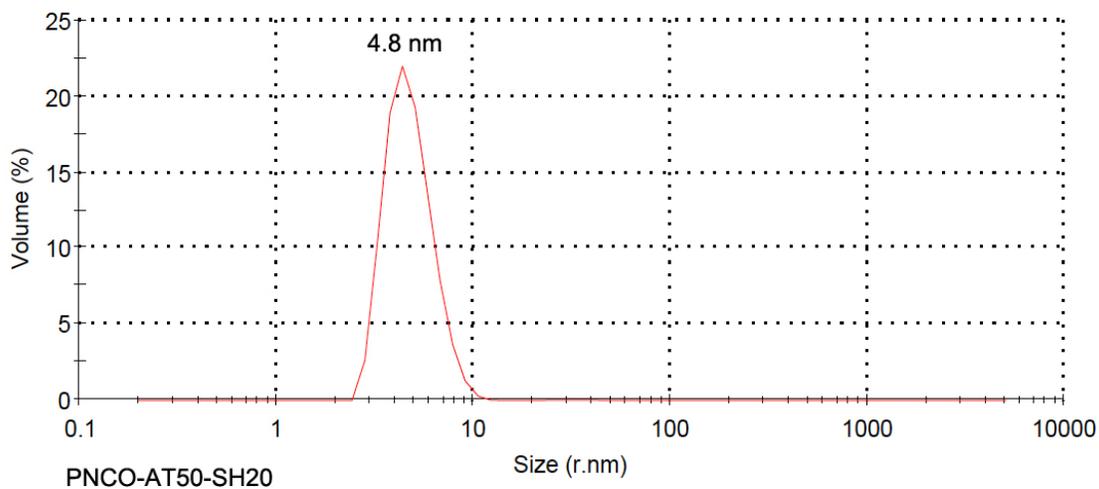
Dynamic Light Scattering Data











Reference

1. Zhang, W. J.; Feng, J.; MacDiarmid, A. G.; Epstein, A. J *Synth Met* 1997, 84, 119-120.