# Supporting Information

# Controlling morphology and crystalline structure in poly(3-hexylselenophene) solutions during aging

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**Synthetic procedures of P3HS.** The P3HS was synthesized by a catalyst-transfer Kumada polycondensation. 2,5-bromo-3-hexylselenophene (1.75 g, 4.7 mmol) was dissolved in THF (50 ml) in a three-neck flask and stirred under $N_2$. After cooling the solution to 0 ˚C, isopropylmagnesium chloride (*i*-PrMgCl) in THF (2.35 mL, 4.7 mmol) was added and the mixture was stirred for 30 min. Then the solution was heated to 35 ˚C and followed by the addition of (1,3-bis(diphenylphosphino)-propane)-dichloronickel(II) Ni(dppp)$Cl_2$ catalyst (0.0675 g, 0.124 mmol). The resulting mixture was stirred at 35 ˚C for 2 h. The reaction was quenched by adding HCl (aq) (50 wt %), and the product was precipitated into methanol and hexane and dried under vacuum to give a deep red solid. The resulted P3HS had molecular weight ($M_n$) of 5600 with PDI of 1.34. $^1$H NMR (500 MHz, $CDCl_3$, δ(ppm)): 7.11 (s, 1H), 2.73 (t, 2H), 1.67 (m, 2H), 1.43 (m, 2H), 0.91 (t, 3H).

**Characterization.** Gel permeation chromatography (GPC) was operated using an Agilent 1260 system equipped with both G1362A refractive-index and G1314A UV detectors (eluent: THF; calibration: polystyrene standards). $^1$H NMR spectra were recorded on a AVANCE III HD 400MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. X-ray diffraction (XRD) was performed on a PANalytical X'Pert PRO X-ray diffractometer using Cu Kα radiation (λ = 1.541 Å) operating at 40 kV and 40 mA. The samples for XRD measurements were prepared by drop-casting P3HS solutions onto silicon wafers followed by evaporation of the solvent at ambient.

**Figure S1**. $^{1}H$ NMR spectrum of the monome

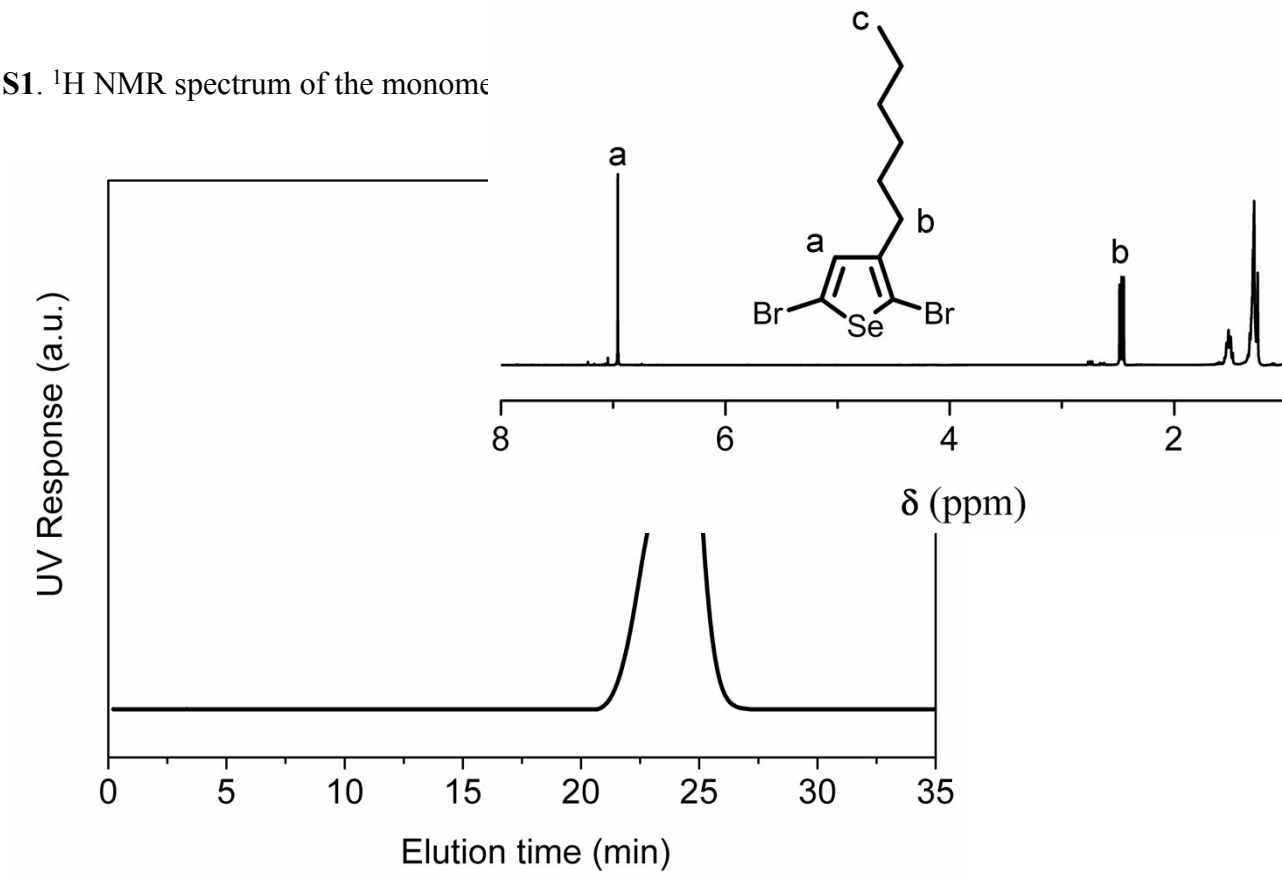


**Figure S2**. GPC profile of P3HS.

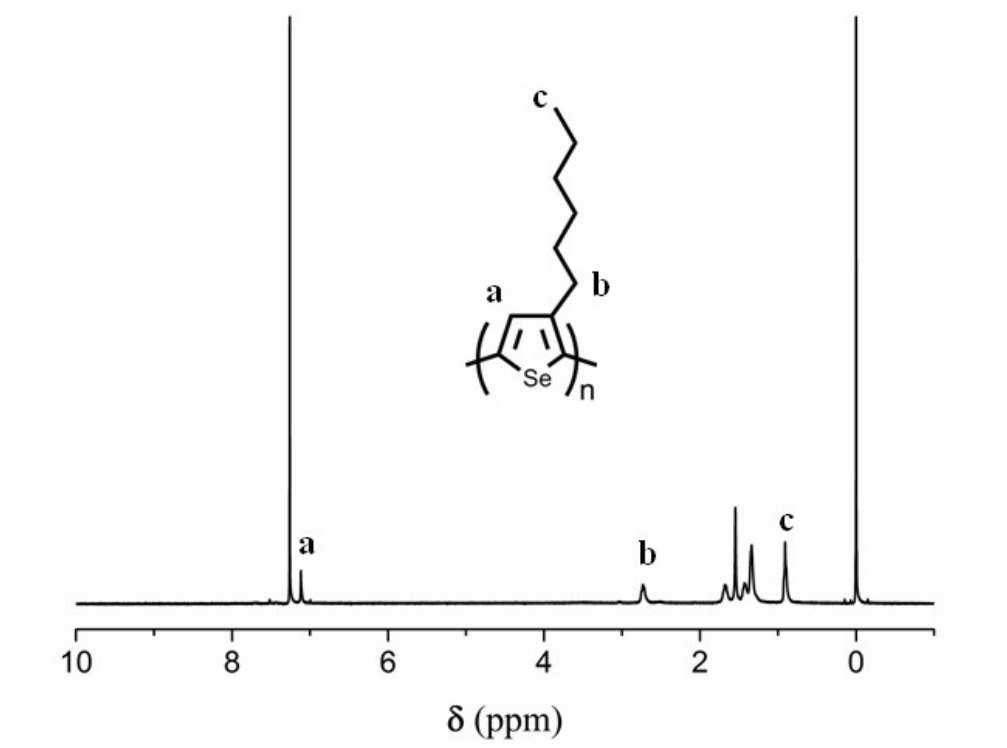


**Figure S3**. $^{1}H$ NMR spectrum of P3HS in $CDCl_3$.

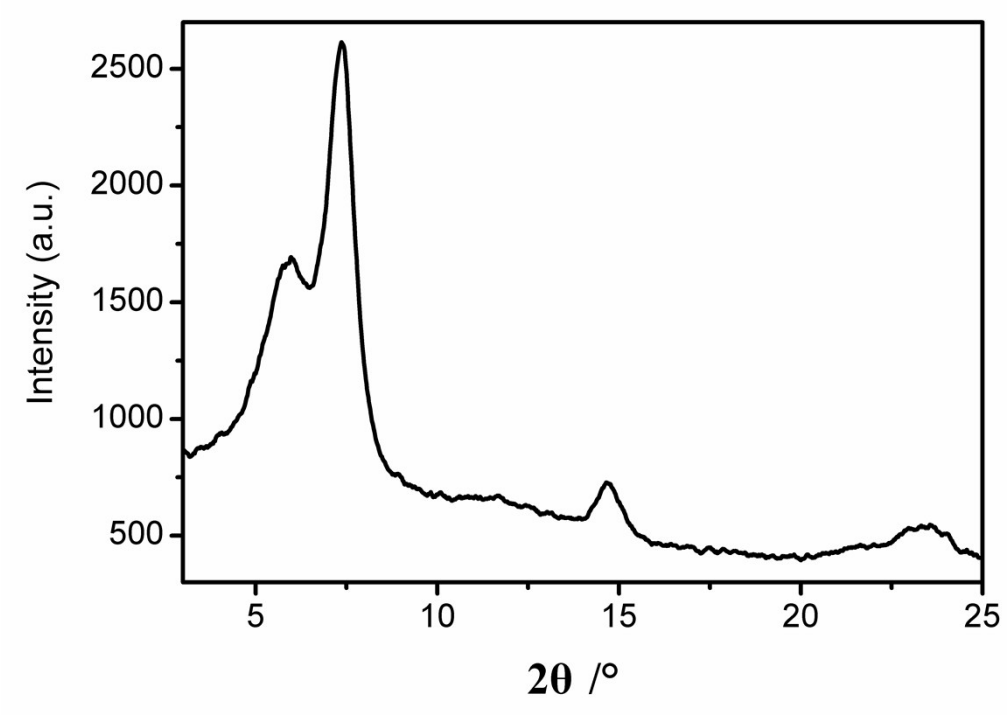


**Figure S4.** XRD profile of P3HS casted from 10 mg/mL $CH_2Cl_2$ solution.