# Supporting Information for:

# Selenium Borohydride Reaction as A Versatile Platform

# for the Straightforward Preparation of Selenide-

# containing Topological Polymers

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### **Experimental Section**

#### Materials

All chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents Co., Ltd. (China). Styrene (St) and methacrylate (MA) were washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with deionized water repeatedly until neutralization. After being dried with anhydrous magnesium sulfate, St and MA were distilled under reduced pressure and kept in a refrigerator at o °C. Vinyl acetate (AR, China Sun Specialty Products Co., Ltd., China) was passed through a neutral alumina column prior to use. Other chemicals were used as received. The xanthate compound 2- (ethoxycarbonothioyl)sulfanyl propanoate (EXEP) was synthesized according to the procedure in the literature.<sup>1</sup>

#### Characterizations

The number-average molecular weights  $(M_n)$  and molecular weight distributions (D) of the polymers were determined by gel permeation chromatography (GPC) conducted on an HLC-8320 GPC equipped with a TSKgel SuperMultiporeHZ-N column (3) (4.6 × 150 mm) at 40 °C. Tetrahydrofuran served as the eluent with a flow rate of 0.35 mL/min. GPC samples were injected using a TOSOH HLC-8320 GPC plus auto sampler. The molecular weights of PS, PVAc and PNVP were calibrated using PS standards, and PMA was calibrated with PMMA standards. Recycling preparative HPLC was performed on an LC-92XX II NEXT Series

equipped with a JAIGEL-2.5HH Column. Tetrahydrofuran served as the eluent with a flow rate of 6 mL/min. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance instrument using CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as an internal standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on an UltrafleXtreme MALDI-TOF mass spectrometer equipped with a 1 kHz smart beam-II laser. The instrument was calibrated prior to each measurement with an external standard of PMMA at the molecular weight under consideration. The compound trans-2-[3-(4-tert-butylphenyl)-2methyl-2-propenylidene]malononitrile (DCTB, Aldrich, > 98 %) served as the matrix and was prepared in CHCl<sub>3</sub> at a concentration of 20 mg/mL. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10:1 (v/v). All samples were dissolved in  $CHCl_3$  at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the plate was inserted into the MALDI mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and to maximize sensitivity. UV-vis spectra were recorded on a Shimadzu UV-3150 spectrophotometer (Shimadzu China, Shanghai, China).

#### Procedures for synthesis of borohydride exchange resin (BER)

Quaternary ammonium anion exchange resin with chloride counterions were stirred with an excess of  $NaBH_4$  in ethanol to obtain BER. The structure was characterized by elemental analysis.

#### Synthesis of selenium-containing polymers

Powdered gray selenium (22 mg) and BER (290 mg) were stirred vigorously in an appropriate solution (2.0 mL) under an argon atmosphere until the solution changed color from brown to pale yellow. The polymer solution was added to the reaction mixture, and a spontaneous reaction occurred (< 5 min), yielding the corresponding selenium-containing polymers. The appropriate solvents for PS and PVAc were N,N-dimethylformamide, while the reactions with PNVP and PMA were conducted in methanol to obtain the corresponding selenium-containing polymers. The contents were dissolved in THF and passed through silica gel to remove contaminants from the resin and then precipitated and purified by re-precipitation. The polymers were obtained by filtration and dried at room temperature under vacuum to a constant weight.  $M_n$  and D were determined by GPC. The chain ends were analyzed by MALDI-TOF mass spectrometry.

### Recycling utilization of selenide-functionalized exchange resin (SeER)

SeER collected after a reaction was scoured three times by tetrahydrofuran to remove attached polymers and then reduced in the presence of sodium borohydride in alcohol. The reduction process was violent and generated gas and heat until the resin changed color from brown to pale yellow.

### Typical procedures for polymerization of styrene

A dry 5 mL ampule was filled with styrene (2.0 mL, 17.79 mmol), ethyl  $\alpha$ bromoisobutyrate (EBiB) (115.0 mg, 0.59 mmol), CuBr (85.0 mg, 0.59 mmol) and N,N,N' N'',N''-pentamethyldiethylenetriamine (PMDETA) (205.5 mg, 1.18 mmol). The solution was deoxygenated by three standard freeze-pump-thaw cycles. The ampule was then flame sealed and placed in an oil bath that was thermoset at the desired temperature. At timed intervals, the ampule was immersed in ice water and then opened. The contents were dissolved in 1 mL of THF. Then, the PS was precipitated into 200 mL of methanol and purified by re-precipitation. The polymer was obtained by filtration and dried at room temperature under vacuum to a constant weight. The conversion of styrene was determined gravimetrically.  $M_n$  and D were determined by GPC. The chain ends were analyzed by the <sup>1</sup>H NMR and MALDI-TOF mass spectrometry.

# Typical procedures for polymerization of methyl acrylate

Using the same procedure used for the preparation of PS, poly(methyl acrylate) was obtained from methyl acrylate (MA) (2 mL, 22.08 mmol), EBiB (42.8 mg, 0.22 mmol), CuBr (31.7 mg, 0.22 mmol) and PMDETA (76.5 mg, 0.44 mmol). PMA was precipitated into hexane and purified by re-precipitation. The polymer was obtained by filtration and dried at room temperature under vacuum to a constant weight. The conversion of MA was determined gravimetrically.  $M_n$  and D were determined by GPC.

# Typical procedures for polymerization of vinyl acetate

A typical procedure for the photo-induced polymerization of vinyl acetate (VAc) with 2-(ethoxycarbonothioyl) sulfanyl propanoate (EXEP) was as follows: VAc (2.0 mL, 21.62 mmol) and EXEP (24.0 mg, 0.11 mmol) were added into a dry 5 mL ampule. The solution was deoxygenated by three standard freeze-pump-thaw cycles. The ampule was sealed and placed under a blue LED lamp (460-470 nm) at 25 °C. At regular intervals, the ampule was immersed in ice water and then opened. The contents were dissolved in THF, precipitated into hexane and

purified by re-precipitation. The polymer was obtained by filtration and dried at room temperature under vacuum to a constant weight. The conversion of VAc was determined gravimetrically.  $M_n$  and D were determined by GPC. The chain ends were analyzed by the <sup>1</sup>H NMR and MALDI-TOF mass spectrometry

# Typical procedures for polymerization of N-vinyl-2-pyrrolidone

Poly(N-vinyl-2-pyrrolidone) was prepared according to the method used for poly(vinyl acetate) using NVP (444.56 mg, 4.00 mmol) and EXEP (4.0 mg, 0.02 mmol). The contents were dissolved in THF, precipitated into diethyl ether and purified by re-precipitation. The polymer was obtained by filtration and dried at room temperature under vacuum to a constant weight. The conversion of NVP was determined gravimetrically.  $M_n$  and D were determined by GPC. The chain ends were analyzed by MALDI-TOF mass spectrometry.

Characterizations of the selenium-containing polymers.

#### **Evolution of GPC traces**



**Figure S1**. Evolution of the GPC traces of the prepared PS-Se-PS obtained from the reaction between SeER and PS-Br with a molecular weight of 3200 g/mol.



**Figure S2**. Evolution of the GPC traces of the prepared PS-Se-PS obtained from the reaction between SeER and PS-RAFT with a molecular weight of 5900 g/mol.



**Figure S3**. <sup>1</sup>H NMR spectra of PVAc-EXEP and PVAc-Se-PVAc.



**Figure S4**. Mass spectra of PVAc-Br ( $M_n$  = 3200 g/mol,  $\mathcal{D}$  = 1.09) and PVAc-Se-PVAc ( $M_n$  = 6200 g/mol,  $\mathcal{D}$  = 1.05).



**Figure S5.** Mass spectra of PNVP-EXEP ( $M_n$  = 3200 g/mol,  $\mathcal{D}$  = 1.09) and PNVP-Se-PNVP ( $M_n$  = 6200 g/mol,  $\mathcal{D}$  = 1.05).



**Figure S6.** Evolution of the GPC traces for PS-Se-PS after treatment with different concentrations of hydrogen peroxide.



**Figure S7.** Evolution of the GPC traces of the prepared PS-Se-PS obtained from recycled SeER.



**Figure S8**. Evolution of the GPC traces of the prepared *cyclic*-PS-Se-PS obtained from the reaction between SeER and Br-PS-Br at a polymer solution concentration of  $1.10 \times 10^{-2}$  mol/L.



**Figure S9.** Analytical GPC traces of cyclic selenium-containing polymers obtained in this study with SeER and Br-PS-Br after recycling GPC purification (THF was used as eluent at a flow rate of 6.0 mL/min).



**Figure S10.** Evolution of the GPC traces of the prepared cyclic polymer obtained from the reaction between SeER and 4PS-Br.



Figure S11. <sup>1</sup>H NMR spectra of 4PS-Br (left) and the figure-eight-shaped polymer (right).



**Figure S12.** (above) Mass spectra of 4PS-Br ( $M_n = 2600$  g/mol, D = 1.05) and (below) the figure-eight-shaped polymer ( $M_n = 1900$  g/mol, D = 1.05) obtained using the NaTFA salt/trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix in positive mode.

# Reference

1. C. Ding; C. Fan; G. Jiang; X. Pan; Z. Zhang; J. Zhu; X. Zhu, *Macromol Rapid Commun* 2015, **36**, 2181-2185.