Supporting Information

Functionalized Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs) via Inverse Vulcanization of Elemental Sulfur and Vinylanilines

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I) Materials and Instrumentation

Sulfur (precipitated, 99.5%-100.5%, Sigma-Aldrich), chloroform-d (CDCl$_3$, 0.01 % v/v TMS Cambridge Isotope Laboratories), methyl sulfoxide-d$_6$ (Acros Organics, 99.9% atom%D), 4-vinylaniline (97%, TCL Chemicals), acryloyl chloride (97%, Sigma-Aldrich), phenyl isocyanate (98%, Sigma-Aldrich), potassium carbonate (99%, Sigma-Aldrich), Those chemicals were used as received. Styrene (99.5%, stabilized, Acros) was purified through an alumina column before use. 

$^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DRX 500 MHz or a BrukerAvance III 400 MHz spectrometer. Chemical shifts are referenced to residual CHCl$_3$ ($\delta$ 7.260 ppm) in CDCl$_3$ and DMSO ($\delta$ 2.500 ppm) in DMSO for $^1$H NMR and residual CHCl$_3$ ($\delta$ 77.0 ppm) for $^{13}$C NMR. Size exclusion chromatography (SEC) was performed in a tetrahydrofuran (THF) mobile phase with a Waters 1515 isocratic pump running three 5-µm PLgel columns (Polymer Labs, pore size 10$^4$, 10$^3$ and 10$^2$ Å) at a flow rate of 1 mL/min with a Waters 2414 differential refractometer and a Waters 2487 dual-wavelength UV-vis spectrometer. Molar masses were calculated using the Empower software (Waters), calibrated against low polydispersity linear polystyrene standards. Rheological analysis was performed on a TA Instruments ARES-G2 and analyzed with the TRIOS software suite.

II) Experimental procedures

1. Poly(S-r-VA) (70 wt% sulfur)  
To a 4 mL glass vial equipped with a magnetic stir bar was added elemental sulfur (700 mg, 2.73 mmol) and heated at 130 °C until a yellow liquid was formed and 4-vinylaniline (0.30 mL, 2.52 mmol) was added to liquid sulfur dropwise. The reaction mixture was stirred at 130 °C for 20 min yielding a red glass. The crude product was purified by column chromatography. Hexanes was used to elute the residual sulfur and the polymer was eluted with THF (0.85 g, yield 85%, conversion of vinylaniline: >99% by NMR, conversion of S$_8$: 78% by flash chromatography).

2. Poly(S-r-VA) (50 wt% sulfur)  
To a 4 mL glass vial equipped with a magnetic stir bar was added elemental sulfur (500 mg, 1.95 mmol) and heated at 130 °C until a yellow liquid was formed and 4-vinylaniline (0.49 mL, 4.20 mmol) was added to liquid sulfur dropwise. The reaction mixture was stirred at 130 °C for 30 min yielding a red glass. The crude product was purified by column chromatography (0.91 g, yield 91%, conversion of vinylaniline: >99% by NMR, conversion of S$_8$: 82% by flash chromatography).

3. Poly(S-r-VPAA)  
Poly(S-r-VA) (70 wt% sulfur, 3.4 g, 8.57 mmol of VA) was dissolved in THF (50 mL) and added the solution of K$_2$CO$_3$ (2.8 g, 20.16 mmol, 2.4 eq) in H$_2$O (12 mL) and acryloyl chloride (1.63 mL, 20.16 mmol,
2.4 eq). The reaction mixture was cooled to 0 ºC in ice bath and stirred for 2 h under Ar. The crude product was concentrated under vacuum and extracted with H₂O (30 mL×4) and methanol (30 mL×2) and dried under vacuum overnight (2.8 g, yield 72%).

4. Poly(S-r-PVPU)
Poly(S-r-VA) (50 wt% S, 200 mg, 0.84 mmol of VA) was dissolved in THF (20 mL) and phenyl isocyanate (0.09 mL, 0.84 mmol, 1 eq) was added. The reaction mixture was stirred at room temperature overnight. The crude product was concentrated under vacuum and extracted with methanol (15 mL×3) and dried under vacuum (260 mg, yield 87%).

5. Preparation of poly(S-r-VPAA) copolymer disc for thermoanalysis
Poly(S-r-VPAA) (400 mg) copolymer was loaded to a diameter = 10 mm die and pressed at 100 ºC in the Hydraulic Press for 30 s to make a disc with 10 mm diameter and 2 mm thickness.

6. Time sweeping rheological analysis of poly(S-r-VPAA)
The rheological analysis was performed on a TA Instruments ARES-G2. The materials were tested on two stainless steel parallel plates with 9.5 mm diameters. Amplitude sweeps, from 0.1% to 100% at 100 rad/s, were performed to determine the limits of the linear viscoelastic (LVE) region. Following this, a 24-hour time sweep, held isothermally at 100 ºC, was performed at a strain within the LVE region, in this case, 3% strain, subject to a 6.28 rad/s angular frequency. All data was managed and analyzed with the TRIOS software suite.

III) Results and Discussion

1. IR analysis of poly(S-r-VA) and poly(S-r-VPAA)

![Figure S1. IR spectra for (i) poly(S-r-VA) and (ii) poly(S-r-VPAA)](image-url)
2. NMR analysis of poly(S-r-VA) before and after addition of D_2O

![NMR spectra](image)

Figure S2. 1H NMR of poly(S-r-VA) in DMSO (bottom) and DMSO-D_2O (2%v/v) (top)

Fig. S2 shows the NMR spectra of poly(Sulfur-random-Vinylaniline) (poly(S-r-Sty) (70 wt% sulfur) in DMSO-\_d_6 before and after the addition of 2 % (v/v) D_2O. The broad peak at 5.3 ppm, represents the -NH_2 group, disappeared after the addition of D_2O due to proton exchange.

3. Stability of poly(S-r-VA) after heat treatment

To test the stability of poly(S-r-VA), the polymer was heated at 120 °C in dichlorobenzene and liquid sulfur for 24 h. The SEC analysis for the products showed similar molecular weight compared before and after heat treatment (Fig. S2).

![SEC data](image)

Figure S3. SEC data for (i) poly(S-r-VA) heated at 120 °C for 24 h in DCB solution (Mn=1043 g/mol, Mw/Mn=1.4) (ii) poly(S-r-VA) (50 wt% S) and S_8 heated at 120 °C for 24 h (Mn=1058 g/mol, Mw/Mn=1.5)

4. SEC analysis of poly(S-r-VA) before and after amidation
The product of amidation of poly(S-\(r\)-VA) with benzyl chloride was analyzed with SEC. The product after amidation poly(Sulfur-\(r\)-random-vinylphenylacryloyl chloride) (poly(S-\(r\)-VPAA) exhibited similar molecular weight (1348 g/mol, Mw/Mn=1.3) with poly(S-\(r\)-VA) (Mn=1038 g/mol, Mw/Mn=1.4). This result suggested the S-S backbone was preserved in the amidation process.

5. NMR analysis of poly(S-\(r\)-PVPU)

The product for poly(S-\(r\)-VA) reacted with isocyanate poly(S-\(r\)-1-phenyl-3-(4-vinylphenyl)urea) (poly(S-\(r\)-PVPU) was characterized by NMR spectra. The bread peaks at 3.3-3.8 ppm represent -S-CH\(_2\)- and 4.0-4.5 represent -S-CH-. The broad peak at 5.0-5.2 ppm, represents the -NH\(_2\) groups in poly(S-\(r\)-VA), didn’t show up in the spectrum of poly(S-\(r\)-PVPU) and a new peak at 8.6-8.7 ppm in the spectrum of poly(S-\(r\)-PVPU) represents the proton in -NH-CO- group.
6. SEC analysis of poly(S-\(r\)-PVPU)

The molecular weight of the product for poly(S-\(r\)-VA) reacted with isocyanate poly(S-\(r\)-1-phenyl-3-(4-vinylphenyl)urea) (poly(S-\(r\)-PVPU) was characterized SEC (Fig. S5) and exhibited similar molecular weight with poly(S-\(r\)-VA).

![SEC data](image)

Figure S6. SEC data for (i) poly(S-\(r\)-PVPU) (Mn=1198 g/mol, Mw/Mn=1.4) (ii) poly(S-\(r\)-VA) (Mn-1349 g/mol, Mw/Mn=1.4)