

## Supporting Information

# Liquid polybutadiene reinforced inverse vulcanised polymers

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## Experimental

### Materials

Sulfur ( $S_8$ , 325 mesh,  $\geq 99.5\%$ , Brenntag UK & Ireland), 1,3-diisopropenylbenzene (DIB, Tokyo Chemical industry), dicyclopentadiene (DCPD, Tokyo Chemical industry), divinylbenzene (DVB, Sigma-Aldrich), liquid polybutadiene (cPBD, Sigma-Aldrich), grade B-1000 liquid polybutadiene (vPBD) was provided by Nisso, and grade LBR-302 liquid polybutadiene (KcPBD) was provided by Kuraray. All chemicals were used without further purification.

### Characterisation

**3-point bending tests** were carried out using the Shimadzu EZ Test at a crosshead speed of 1 mm/min at 25 °C, with a span of 60 mm between the supports. Specimens were 15 mm wide, 4 mm thick and 100 mm long and were tested according to ISO 178.

**Charpy impact tests** were carried out using Zwick Roell HIT5P with a 1J hammer. The unnotched specimens were 10 mm wide, 4 mm thick and 80 mm long and were tested according to ISO 179-2.

**Vickers hardness tests** were carried out using Mitutoyo hardness testing system at room temperature with a 2 kg load (HV2) on specimens that were 10 mm wide, 5 mm thick and 55 mm long and were tested according to ISO 6507. Specimens were polished using sandpaper grits of P280, P400, P800, and P1200 to provide a smooth surface for the tests.

**Differential scanning calorimetry (DSC)** thermograms were obtained using TA DSC25, where heat-cool-heat cycles were carried out with temperature ranges of -50 – 150 °C for sulfur polymers, and -90 - 50 °C for LPBD under nitrogen. The heating rate was 10 °C/min and the cooling rate was 10 °C/min.

**Fourier Transform Infrared Spectroscopy (FTIR)** was performed with a Bruker Vertex V70 FTIR spectrometer, with a diamond ATR crystal. Polymers were analysed as sheets with a thickness of 0.1 - 0.5 mm, made using a hot press at 160 °C, 5 MPa for ~5 min.

**Thermogravimetric analysis (TGA)** was carried out using TA Instruments Discovery TGA550 with wire wound (Pt/Rh) furnace at a ramp rate of 10 °C/min to 600 °C, and for LPBD to 1000 °C under nitrogen purge gas.

**Nuclear magnetic resonance (NMR)** was carried out using Bruker Ultrashield 400MHz with samples at a concentration of 37 g/L. Chemical shifts were referenced to residual  $CHCl_3$  ( $\delta 7.26$  ppm) in  $CDCl_3$ .

**Size exclusion chromatography (SEC)** was conducted using a Malvern Viscotek TDA 302 instrument equipped with a triple detector array TDA 305. SEC was performed at 35 °C at a flow rate of 1 mL min<sup>-1</sup> using THF as the mobile phase. Samples were analysed using a conventional calibration based upon linear poly(styrene) standards of  $M_p$  1200, 2430, 5640, 12630 and 29100.

**Scanning electron microscopy (SEM)** imaging of the polymer morphology was achieved using a Hitachi S-4800 cold Field Emission Scanning Electron Microscope (FE-SEM) operating in both scanning and transmission modes. The dry samples were prepared by adhering the polymer monoliths to a SEM stub with silver paint. Samples were coated with a 5-10 nm thick layer of chromium by a Quorum sputter coater using a current of 120 mA. Imaging was conducted at a working distance of ~6 mm at 5 kV. Images were taken using a combination of both upper and lower detector signals.

### Synthesis of S-DIB

Sulfur (5 g, 0.16 mol) and DIB (5 g, 0.031 mol) were added to a 40 mL reaction vial and heated at 160 °C in a heating block on a hot plate while stirring at 900 rpm. The mixture changed from yellow to a dark red viscous mixture after 30 min and was poured out into a silicone mould. The polymer was placed into the oven to cure at 140 °C for ~20 h. A black brittle polymer was produced.

### Synthesis of S-DVB

Sulfur (5 g, 0.16 mol) and DVB (5 g, 0.038 mol) were added to a 40 mL reaction vial and heated at 160 °C in a heating block on a hot plate while stirring at 900 rpm. The mixture changed from yellow to a dark orange viscous mixture after 10 min and was poured out into a silicone mould. The polymer was placed into the oven to cure at 140 °C for ~20 h. A black brittle polymer was produced.

#### Synthesis of S-DCPD

Sulfur (40 g, 1.28 mol) and DCPD (40 g, 0.304 mol) were added to a 250 mL round bottom flask and heated at 160 °C in a heating block on a hot plate while stirring at 900 rpm. The mixture changed from yellow to a black viscous mixture after 1 h 30 min and was poured out into a silicone mould. The polymer was placed into the oven to cure at 140 °C for ~20 h. A black brittle polymer was produced.

#### Synthesis of S-DIB-PBD

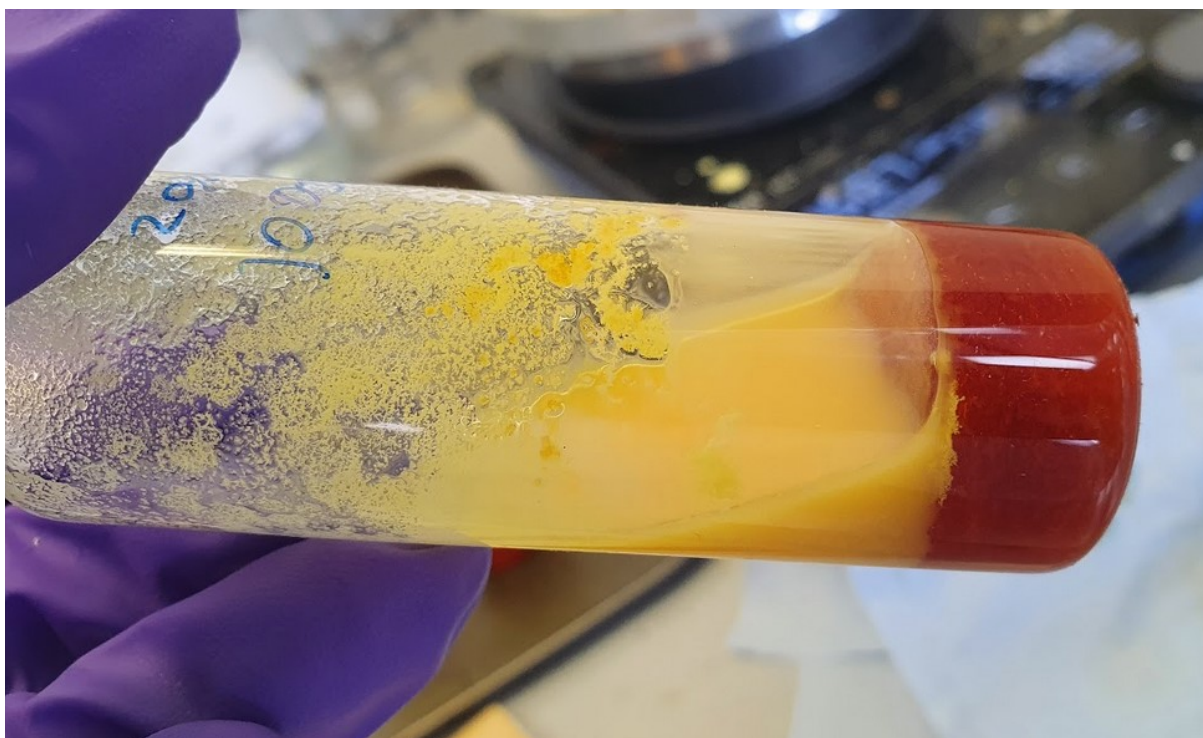
Sulfur (5 g, 0.16 mol) and L-PBD were added to a 40 mL reaction vial and heated at 160 °C in heating block on a hot plate with stirring at 900 rpm. The mixture changed from a yellow to a viscous opaque ochre mixture after 15 min. DIB was added to the mixture and after 10 – 15 min, the viscosity increased and the colour changed to dark brown then it was poured out into a silicone mould. The polymer was placed into the oven to cure at 140 °C for ~20 h. A black opaque polymer was produced.

#### Mechanical test sample preparation

All S-DIB-PBD samples were hot pressed in metal moulds at 160 °C for approximately 20 - 30 min, S-DIB was hot pressed at 120 °C for 10-20 min, S-DVB was hot pressed at 160 °C for 10-20 min, and S-DCPD was used straight from the silicone mould after curing as the stress of the temperature change after hot pressing caused it to crack.

**Table S1** Sample compositions.

Sample abbreviation	Sulfur content (wt.%)	Crosslinker	Crosslinker content (wt.%)	LPBD	LPBD MW (g/mol)	LPBD content (wt.%)
cPBD	N/A	N/A	N/A	<i>cis</i> -1,4 Sigma LPBD	15413	100
vPBD	N/A	N/A	N/A	1,2-vinyl Nisso LPBD	3620	100
KcPBD	N/A	N/A	N/A	<i>cis</i> -1,4 Kuraray LPBD	5690	100
S-cPBD	50	N/A	N/A	<i>cis</i> -1,4 Sigma LPBD	15413	50
S-DIB	50	1,3-diisopropenylbenzene	50	N/A	N/A	N/A
S-DIB-10cPBD	50	1,3-diisopropenylbenzene	40	<i>cis</i> -1,4 Sigma LPBD	15413	10
S-DIB-20cPBD	50	1,3-diisopropenylbenzene	30	<i>cis</i> -1,4 Sigma LPBD	15413	20
S-DIB-30cPBD	50	1,3-diisopropenylbenzene	20	<i>cis</i> -1,4 Sigma LPBD	15413	30
S-DVB	50	divinylbenzene	50	N/A	N/A	N/A
S-DCPD	50	dicyclopentadiene	50	N/A	N/A	N/A



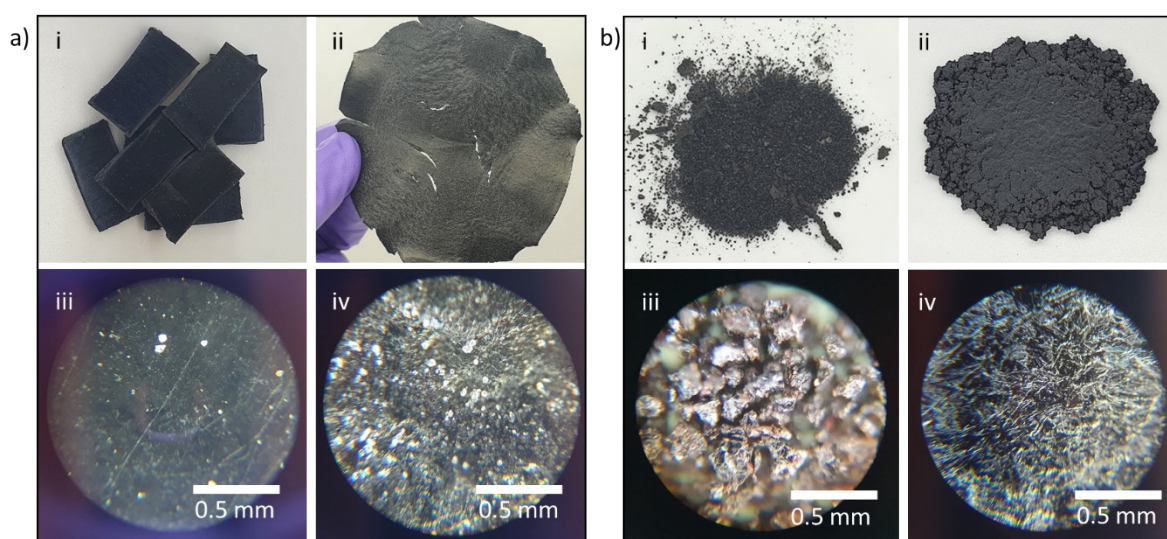
**Fig. S1** Photo of S-DIB-20vPBD separation after addition of DIB.



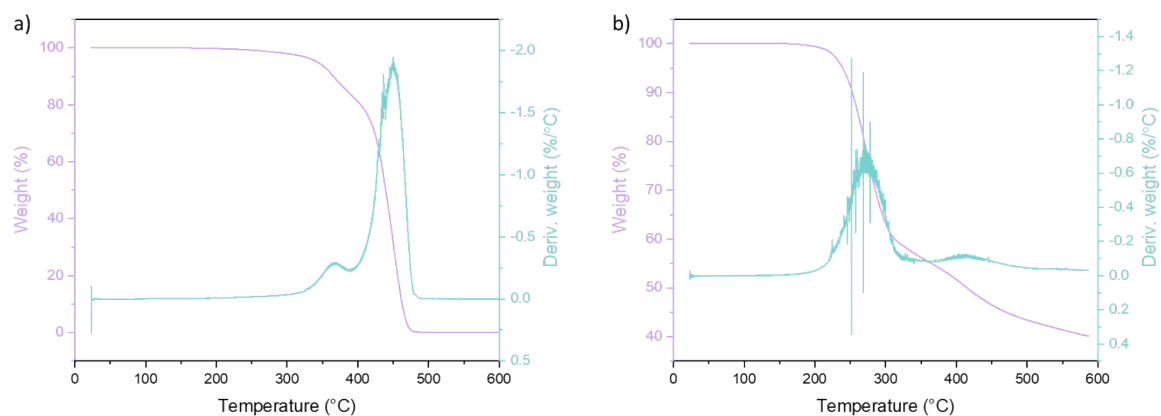
**Fig. S2** Photo of S-DIB-VPBD pre-polymer when Zn catalyst was used.



**Fig. S3** Photos of S-DIB-cPBD pre-polymer a) when DIB is reacted before cPBD; b) when cPBD is reacted before DIB.



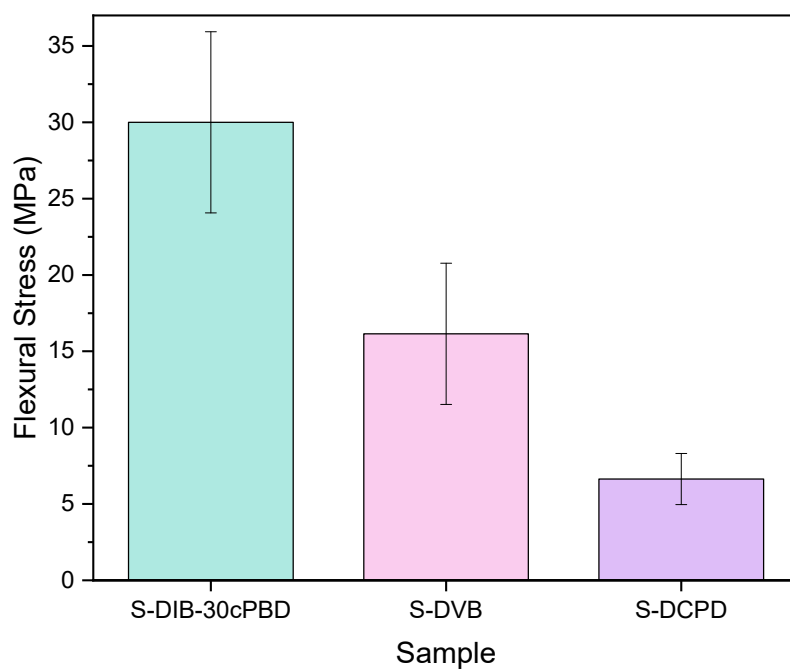
**Fig. S4** Photos of a) vulcanised rubber and b) S-DIB-30cPBD; i) before hot pressing, ii) after hot pressing at 160 °C. Optical microscope images taken using 10x magnification lens iii) before hot pressing, iv) after hot pressing at 160 °C to show the recyclability of S-DIB-30cPBD by comparing it to a non-recyclable material.



**Fig. S5** TGA curves of a) cPBD and b) S-cPBD to show the derivative weight to highlight the two-step degradation of cPBD that occurs.

**Table S2** DSC and TGA values of different sulfur polymer samples.

Sample	$T_g$ (°C)	Onset temperature (°C)	End temperature (°C)	Weight loss (%)
cPBD	-	414	467	99.7
S-cPBD	-	321	387	97.8
S-DIB	34	221	278	68.3
S-DIB-10cPBD	16	185	275	47.1
S-DIB-20cPBD	42	247	306	47.8
S-DIB-30cPBD	78	247	306	54.7



**Fig. S6** Bar chart of the flexural stress of S-DIB-30cPBD compared to other sulfur polymers.

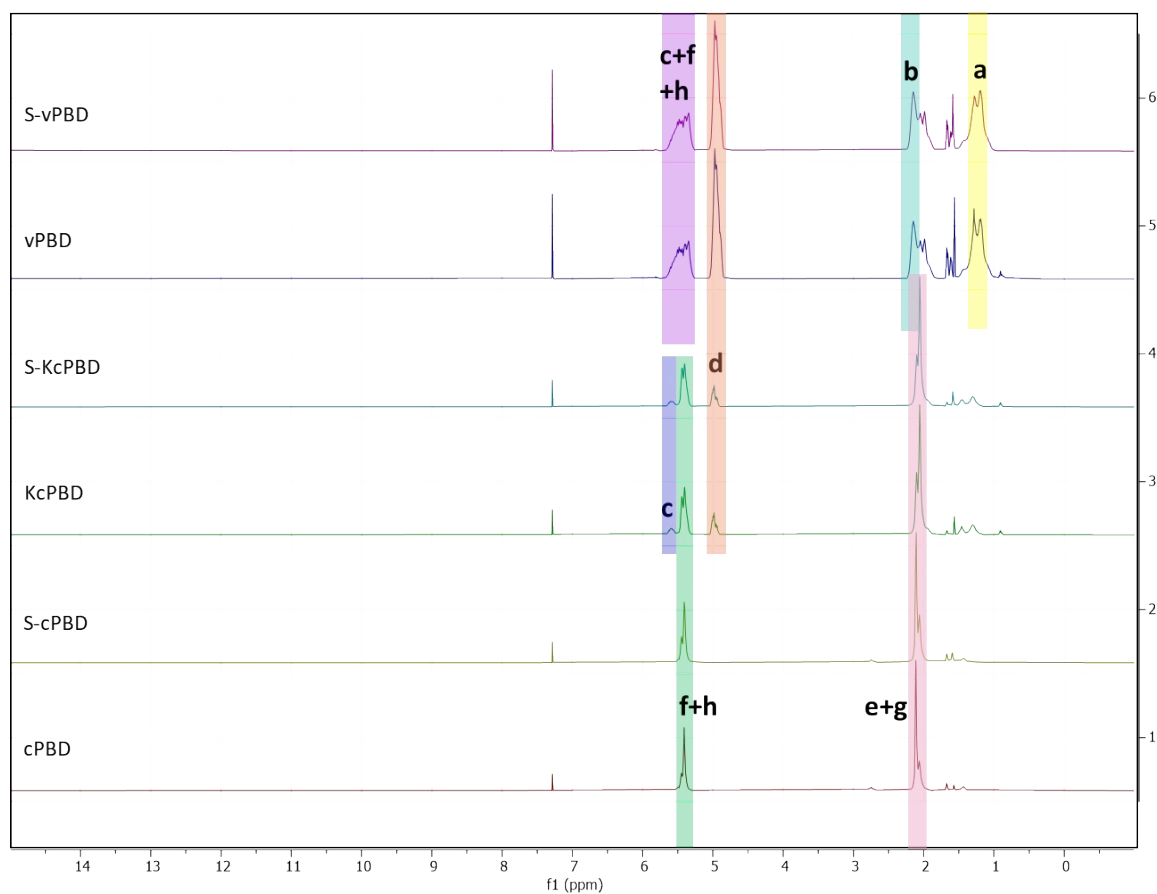
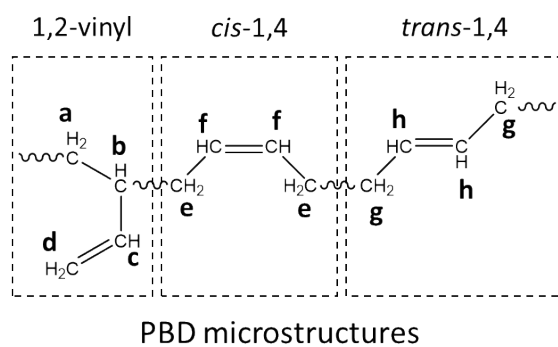
**Table S3** 3-point bending test results of different sulfur polymers.

Sample	Flexural Stress (MPa)	Flexural Modulus (MPa)	Stroke (mm)
S-DIB	3.93	1377	0.46
S-DIB-10cPBD	3.00	355	1.19
S-DIB-20cPBD	16.41	2152	1.09
S-DIB-30cPBD	30.00	1584	2.26
S-DVB	16.14	2402	0.83
S-DCPD	6.64	2156	0.56

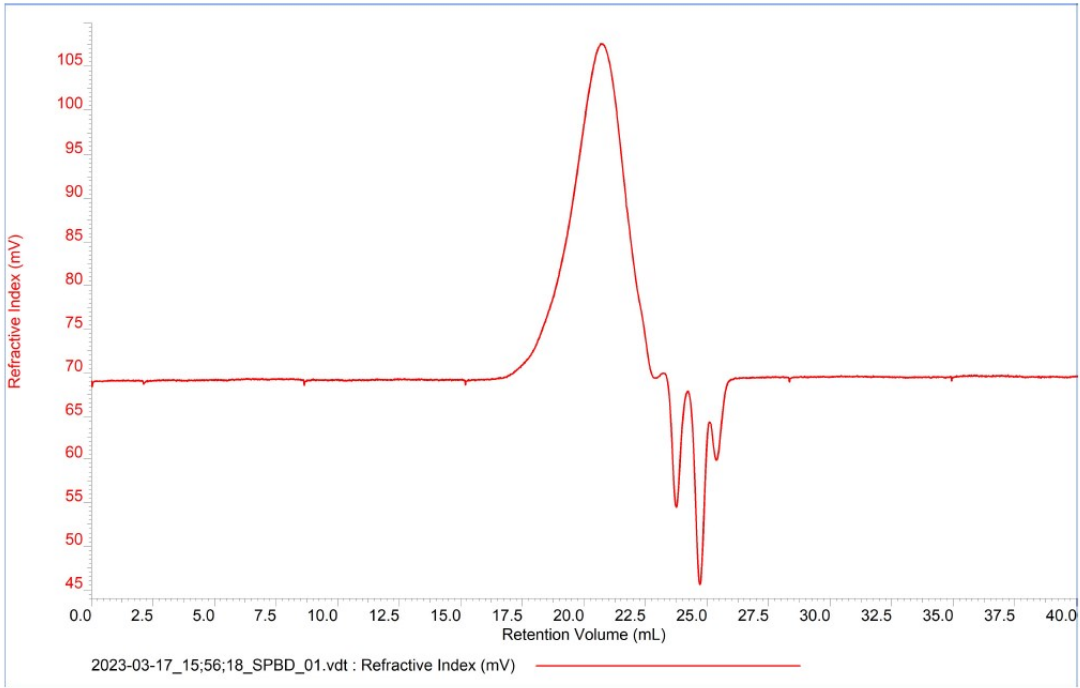
**Table S4** Elemental analysis of sulfur polymers.

Sample	C (%)	H (%)	S (%)
S-DIB	43.32	4.11	51.45
S-DIB-10cPBD	42.77	4.23	52.1
S-DIB-20cPBD	41.85	4.4	51.86
S-DIB-30cPBD	42.27	4.66	52.26



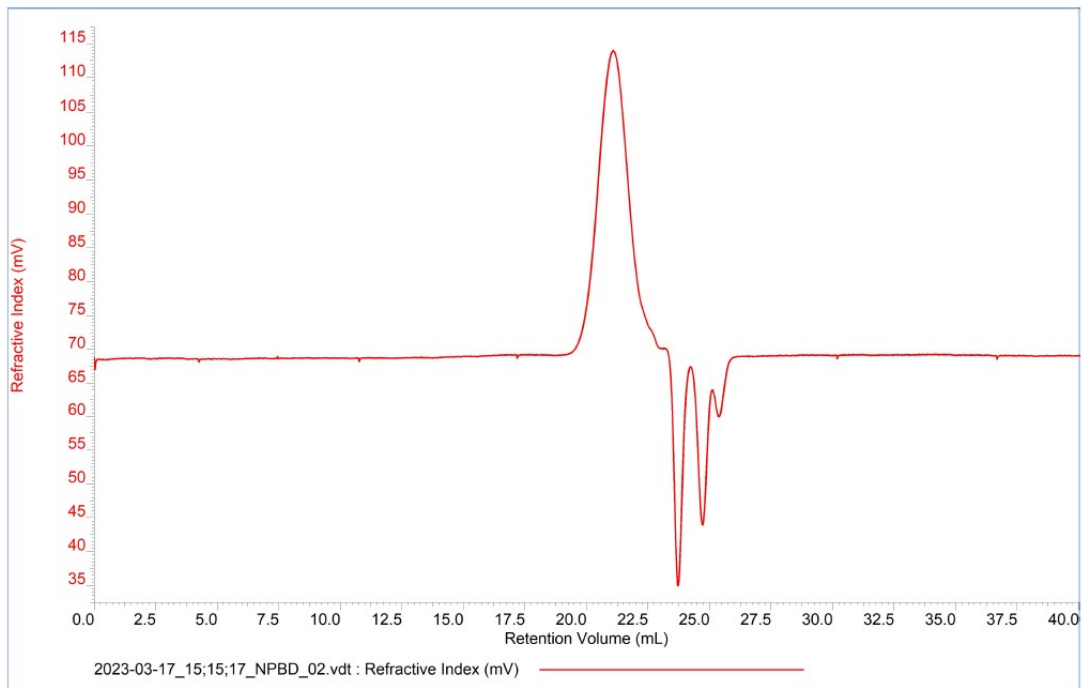


**Fig. S7** <sup>1</sup>H NMR spectra of each type of LPBD compared to their corresponding S-LPBD pre-polymer. No change in spectra between the LPBD and S-LPBD for each type of LPBD indicates that once reaction with sulfur occurs, a sufficient amount of crosslinking occurs that S-LPBD becomes insoluble and that we are likely observing the unreacted LPBD in the spectra of S-LPBD samples.



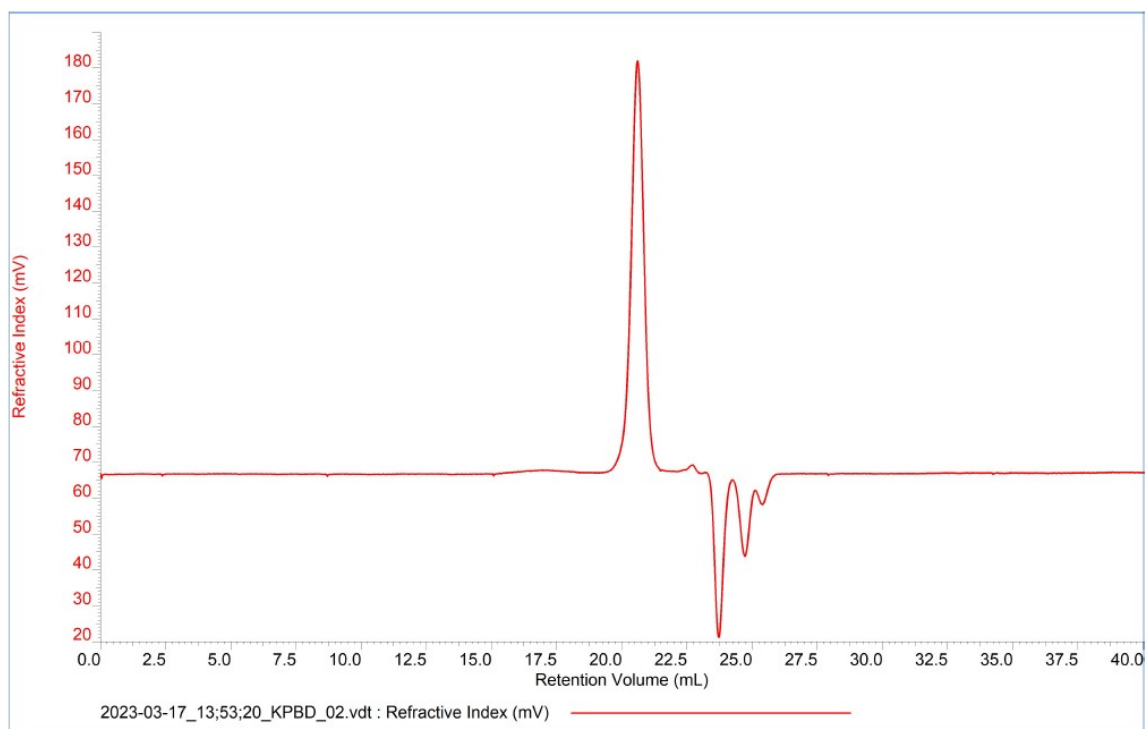
Peak	Ret Time	Mn	Mw	Mp	Mw/Mn	RI Area
1	20.717	3,104	15,413	4,596	4.965	95.89

**Fig. S8** SEC of cPBD.



Peak	Ret Time	Mn	Mw	Mp	Mw/Mn	RI Area
1	21.073	2,053	3,620	2,955	1.763	64.29

**Fig. S9** SEC of vPBD.



Peak	Ret Time	Mn	Mw	Mp	Mw/Mn	RI Area
1	20.597	5,117	5,690	5,320	1.112	67.53

**Fig. S10** SEC of KcPBD.