Electronic Supplementary Material (ESI) for Polymer Chemistry. This journal is © The Royal Society of Chemistry 2023

# Supporting information

## **Raman Analysis of Inverse Vulcanised Polymers**

Liam J. Dodd, Cássio Lima, David Costa-Milan, Alex R. Neale, Benedict Saunders, Bowen Zhang, Andrei Sarua, Royston Goodacre, Laurence J. Hardwick, Martin Kuball, Tom Hasell

Department of Chemistry, University of Liverpool, Crown St, Liverpool, L69 7ZD, United Kingdom

## **Table of Contents**

I. General Considerations	S2
II. Polymer Syntheses	S3
III. Synthesis and Characterisation of Gold Nanoparticles	S5
IV. Raman Spectra of Polymer Samples Using Conventional Raman Methods and SERS	<b>S</b> 6
V. UV/Vis Spectra of the Crosslinkers	<b>S</b> 8
VI. Fluorescence Spectra of the Crosslinkers	S9
VII. Absorption Spectra and Tauc Plots of the Polymer Thin Films	S11
VIII. Fluorescence Spectra of the Polymer Thin Films	S13
IX. Screening of Different Raman Spectroscopic Techniques	S20
X. Evidence of Oxidation of Inverse Vulcanised Polymers	S24
XI. DSC Thermograms for the Second Batch of Polymers	S27
XII. 1064 nm SERS Spectra for DVB Polymers	S28
XIII. Density Functional Theory Calculation Method	S29
XIV. Additional Calculated Data for the Polymer Models	S32
XV. Parameterisation of the Predicted Spectra	S35
XVI. Step by Step Guide for the Quantification of Dark Sulfur by Raman Spectroscopy	S37
XVII. Calculation of the Expected Sulfur Rank	S38
XVIII. Step by Step Guide for Determining the Sulfur Rank by Raman Spectroscopy	S40
XIX. DIB Case Study Band Deconvolution Data	S42
XX. DIB Case Study	
XXI. References	S43

#### I. General considerations

All chemicals were used as received. All Chemicals were obtained from Sigma Aldrich unless otherwise specified. Ground sulfur sublimed powder reagent grade ≥99.5 % was obtained from Brenntag UK & Ireland. Dicyclopentadiene (stabilised with BHT) [precursor to Cyclopentadiene] >97%, and 1,3-Diisopropenylbenzene (stabilised with TBC) >97% were obtained from Tokyo Chemicals Industry. CHNS combustion microanalyses were performed on an elementar Vario Micro cube, with a first analysis performed to acquire rough data that was then used to calibrate the instrument for a second, more accurate analysis. Differential scanning calorimetry was performed on a TA instruments DSC25 discovery series equipped with an RCS90 and using Tzero aluminium hermetic pans and aluminium lids, in the heating range -90 °C to 150 °C, at a heating rate of 10 °Cmin<sup>-1</sup> and a cooling rate of 5 °Cmin<sup>-1</sup>. UV/Vis spectra were obtained using a CARY 5000 UV-Vis-NIR spectrophotometer. Fluorescence measurements were performed on an Edinburgh instruments Fluorescence Lifetime Spectrometer 980, with excitation using a xenon lamp and detection using a photon multiplier tube. Raman spectra were obtained using one of the following instruments: for handheld 1064 nm Raman, a Snowy Range Instruments model CBex 1064 was used; for all other 1064 nm Raman, a Metrohm i-Raman EX 1064 was used; for 532 nm and 785 nm Raman, an inVia Reflex Qontor Confocal Raman Microscope was used.

## **II. Polymer Syntheses**

## **II.A. General Method**

Inverse vulcanisation reactions are particularly sensitive to their reaction conditions, so great care was taken to ensure consistency in the reaction method. The same hotplate and thermocouple were used for every reaction. The hotplate was equipped with an aluminium heating pan and block and to protect the reaction vials from the variable conditions in the laboratory, the heating pan, heating block and reaction vials were wrapped tightly in an excess of aluminium foil. Sulfur (3, 5, or 7 g  $\pm$  0.0099 g) was melted at a desired temperature in a 40 mL reaction vial, without a lid, with 200 rpm stirring from a 14 mm cross shaped stirrer. The system was left for 10 to 20 mins to allow thermal equilibration. The selected crosslinker (3, 5, or 7 g  $\pm$  0.0099 g) was poured into the 40 mL reaction vial, to give a reaction of 10 g scale, and the stirring rate was immediately increased to 900 rpm. The reaction was monitored by dip testing: when an aliquot of the reaction was removed on the end of a spatula, and the aliquot remained a single phase upon cooling, (that is no sulfur precipitated) the reaction solution was poured into a preheated mould and left in the oven at 135 °C overnight to cure. Note that dip testing was not successful for DVB polymers as there was no point at which the aliquot would remain a single phase, but at the same time leave the reaction solution of low enough viscosity to pour. Where necessary, cured polymers were ground to powder.

Name		DVB			DIB		DCPD				Squalene					
Chemical structure				(		-										
Synthesis at		135 °C			135 °C			135 °C			160 °C			170 °C		
Feed ratio																
Crosslinker (%)	30	50	70	30	50	70	30	50	70	30	50	70	30	50	70	
Sulfur (%)	70	50	30	70	50	30	70	50	30	70	50	30	70	50	30	
Microanalysis																
C expected (%)	27.7	46.1	64.6	27.3	45.5	63.8	27.3	45.4	63.6	27.3	45.4	63.6	26.3	43.9	64.4	
C actual (%)	21.4	26.1	50.9	8.5	22.6	36.7	11.7	16.2	10.2	17.6	28.2	32.6	38.1	48.2	61.3	
H expected (%)	2.3	3.9	5.4	2.7	4.5	6.2	2.8	4.6	6.4	2.8	4.6	6.4	3.7	6.1	8.6	
H actual (%)	1.7	2.1	4.1	0.9	2.2	3.3	1.5	1.7	1.5	1.8	2.6	3.1	4.8	6.3	8.3	
S expected (%)	70.0	50.0	30.0	70.0	50.0	30.0	70.0	50.0	30.0	70.0	50.0	30.0	70.0	50.0	30.0	
S actual (%)	76.9	71.4	44.3	90.5	75.7	59.7	88.8	82.9	88.9	82.0	69.4	64.8	56.5	45.3	29.9	
Glass transition																
temperature	39.2	51.0	97.2	4.9	12.6	36.8	20.1	38.4	11.8	47.6	83.5	93.0	18.2	33.2	19.0	
from DSC / °C																

Table S1: Synthetic conditions and analyses of the first batch of inverse vulcanised polymers



Figure S1: Representative DSC thermograms of the first batch of inverse vulcanised polymers.

#### **II.B.** Thin Films

To make thin films, rather than pouring the pre-polymer into a pre-heated mould, it was poured onto a preheated quartz slide. This slide was suspended on silicone blocks at its ends, so that the minimum surface area was in contact with another surface: when the quartz slide was in contact with the oven tray, polymer leaked to the underside, fusing the quartz slide to the tray. A second preheated quartz slide was then lay upon the top of the first, flattening the pre-polymer into a thin fil. A gentle pressure was exerted on the top of the assembly by hand using tweezers, in order to squeeze out any air bubbles and thin out the film. This had to be done with care, as if the upper slide shifted over the lower one, the film would be ruined. The assembly was then returned to the oven to cure. This process was difficult to perform, and required perfect timing for the pouring of the polymer: too early, and sulfur would precipitate upon the quartz slide and bubble formation would be promoted by the remaining unreacted crosslinker that could volatilise, too late and the polymer would be too viscous to form a thin film. Pouring had to be done rapidly to prevent excessive cooling of the reaction solution. The perfect quantity of polymer had to be poured onto the quartz plate: too much and the film could be too thick or polymer would obscure the outer faces of the slide, too little and the film could be too thin, or could promote the formation of bubbles. Even with perfect film making technique, some bubbles were usually present in the film. This was unavoidable, and if the bubbles were dispersed in such a way that no sufficiently large area of the film was left unaffected and suitable for analysis, then the sample had to be discarded. Some polymer usually accumulated as hanging drops on the underside of the quartz plate during curing, which were then solidified in place. These could be removed by placing the film into a freezer to embrittle the polymer, after which it could be chiselled off with the flat end of a spatula.

#### **II.C. Under Atmosphere Reactions**

For the cases of DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air, while the sulfur was thermally equilibrating, the reaction vial was sealed with a septum and then purged with nitrogen or compressed air for ten minutes, after which time, active gas flow was removed and a gas balloon of either nitrogen or compressed air was added to the septum. The reactions could not be left under active purge while the crosslinker was present as the gas flow removed the volatilised crosslinker, promoting further crosslinker evaporation, quickly removing all crosslinker. The crosslinker was purged with nitrogen or compressed air for two minutes before it was syringe injected into the reaction vial. The stirring was then increased to 900 rpm and the reactions were left to vitrify and then cure on the hotplate overnight. Oven curing was not suitable as a nitrogen atmosphere could not be implemented.

## III. Synthesis and Characterisation of Gold Nanoparticles

## **III.A. Spherical Gold Nanoparticles**

Spherical gold nanoparticles were synthesized by the citrate synthesis method.<sup>1</sup> Aqueous sodium citrate (1.4 mL, 38.8 mM) was quickly added to aqueous HAuCl<sub>4</sub> (200 mL, 2.53x10<sup>-4</sup> M) which was already under reflux. The refluxing solution was stirred for 30 min until a clear red solution was obtained. ICP analysis of the solution indicated the purity of the solution: it contained only gold metal in exactly the predicted concentration. The UV/Vis spectrum indicated a plasmon band at 534 nm. The nanoparticle solution was concentrated by centrifugation before use in SERS.



Figure S2: UV/Vis of the spherical gold nanoparticle solution.

## **III.B. Gold Nanorods**

Gold nanorods were synthesized by the method described by Vidgerman and Zubarev<sup>2</sup>. To 10 mL of a HAuCl<sub>4(aq)</sub> (5 mM) and hexadecyl trimethylammonium bromide (100 mM) solution, 460  $\mu$ L of a NaOH<sub>(aq)</sub> (10 mM) and NaBH<sub>4(aq)</sub> (10 mM) was added with rapid stirring to make the seed solution. To 10 mL of a HAuCl<sub>4(aq)</sub> (5 mM) and hexadecyl trimethylammonium bromide (100 mM) solution, 70  $\mu$ L of an AgNO<sub>3(aq)</sub> (100 mM) solution, and 700  $\mu$ L of a hydroquinone (100 mM) solution was added with rapid stirring. To this solution, 160  $\mu$ L of the seed solution was added with rapid stirring, which continued overnight. ICP analysis of the solution indicated the purity of the solution: it contained only gold metal in just below the expected concentration. The UV/Vis spectrum indicated a plasmon band at 1044 nm.



Figure S3: UV/Vis of the gold nanorod solution.



## IV. Raman Spectra of Polymer Samples Using Conventional Raman Methods and SERS

Figure S4: Raman spectra of inverse vulcanised polymers obtained with a 785 nm excitation laser wavelength.



**Figure S5**: Raman spectra of inverse vulcanised polymers obtained with a 532 nm excitation laser at 0.1 % power and a 10 s exposure time.



**Figure S6**: Raman spectra with 532 nm excitation laser with different laser intensities, analysing DVB50-S50 with a 10 s exposure time.



**Figure S7**: Raman spectra with 532 nm excitation laser, using 0.1 % intensity, with a 10 second exposure time from a 50x objective lens, for different polymers coated with gold nanoparticles. The inset image is of a DVB50-S50 polymer surface coated with gold nanoparticles. Several different laser intensities were tried with different focal points which had different concentrations of gold nanoparticles, all of which failed to give a spectrum.

## V. UV/Vis Spectra of the Crosslinkers



**Figure S8**: UV/Vis spectra of the crosslinkers, diluted in chloroform to the following v/v concentrations: 0.001 % DVB, 0.001 % DIB, 0.5 % DCPD and 0.01 % squalene. Data below 400 nm may not be reliable due to an unreliable baseline.

## VI. Fluorescence Spectra of the Crosslinkers



**Figure S9**: Fluorescence spectra of a 0.00001 % v/v solution of DVB in chloroform. Note that DVB is a mixture of the para and meta isomers, and is 80 % pure, with most of the impurity being the para and meta isomers of ethyl styrene. This combination of components may explain the complexity of this spectrum relative to that of DIB.



Figure S10: Fluorescence spectra of a 0.0001 % v/v solution of DIB in chloroform.



Figure S11: Fluorescence spectra of a 0.1 % v/v solution of DCPD in chloroform.



Figure S12: Fluorescence spectra of a 0.1 % v/v solution of squalene in chloroform.

#### VII. Absorption Spectra and Tauc Plots of the Polymer Thin Films

Firstly, the UV/Vis of the unreacted crosslinkers showed no absorbance in the visible region; expected since they are clear colourless liquids. All however did show absorbance at UV wavelengths (see the supporting information, Section V). From these UV absorptions, fluorescence spectroscopy was performed, the spectra of which are provided in the supporting information, Section VI. DIB and DVB were found to be very effective at fluorescence, whereas DCPD and squalene were very poor at fluorescence, though they did provide some nominal signal. Crucially, all of the crosslinkers only fluoresced when excited with UV wavelengths, and only fluoresced in the UV region of the spectrum, suggesting that leftover unreacted crosslinker is not responsible for the observed fluorescence of the inverse vulcanised polymers, and it is the polymers themselves that fluoresce when under Raman analysis.

With this conclusion, the polymers were studied by UV/Vis and fluorescence spectroscopy. Because blocks and powders of the polymers gave too strong a signal in UV/Vis, thin films of polymer were created (Figure S13, see the supporting information, Section II.B. for details). UV/Vis spectra (Figure S14) were obtained in the region of 235 nm to 1100 nm, to cover the range of Raman excitation laser wavelengths that were accessible in this study. In general, as shown in Figure S14, the polymers showed negligible absorbance at longer wavelengths, but as the wavelength was decreased, the absorbance began to increase, rapidly rising to the detector limit in the UV.

ま	DVB	DIB	DCPD 135 °C	DCPD 160 °C	Squalene	Polymer	Film Thickness / µm	Absorption Coefficient at 1064 nm / cm <sup>-1</sup>	Wavelength where absorption coefficient becomes > 0.5 cm <sup>-1</sup>	Tauc plot direct band gap / eV
		1		L	1	DVB30-S70	60	-1.58×10 <sup>-2</sup>	696 nm	2.91
a 16 200/						DVB50-S50	50	-2.90×10 <sup>-2</sup>	757 nm	2.92
Sulfur 30%	CO I	CO		$\mathbf{x}$		DVB70-S30	40	-0.98×10 <sup>-2</sup>	862 nm	2.72
						DIB30-S70	40	-5.80×10 <sup>-2</sup>	729 nm	2.45
	1000					DIB50-S50	60	-5.22×10 <sup>-2</sup>	757 nm	2.48
			1	1		DIB70-S30	30	-10.17×10 <sup>-2</sup>	762 nm	2.99
	± 1	+	\$	8	- E	DCPD30-S70-T135	20	-4.49×10 <sup>-2</sup>	956 nm	2.88
Sulfur 50%	20	do			00	DCPD50-S50T-135	40	0.13×10 <sup>-2</sup>	1018 nm	2.87
						DCPD70-S30-T135	20	12.79×10 <sup>-2</sup>	1072 nm	2.91
	<u> </u>					DCPD30-S70-T160	80	0.61×10 <sup>-2</sup>	894 nm	2.89
	er					DCPD50-S50-T160	90	3.19×10 <sup>-2</sup>	922 nm	3.03
	1		+	+		DCPD70-S30-T160	80	5.58×10 <sup>-2</sup>	963 nm	2.93
Sulfur 70%	王		æ	æ	60	Squalene30-S70	50	6.15×10 <sup>-2</sup>	989 nm	2.21
	00					Squalene50-S50	50	0.77×10 <sup>-2</sup>	957 nm	2.63
	6	and the second				Squalene70-S30	80	2.13×10 <sup>-2</sup>	946 nm	2.30

Figure S13: A photograph of inverse vulcanised polymer thin films as well as tabulated assorted spectral data regarding the UV/Vis of the films. The polymer films are adhered between two 2.5 cm by 2.5 cm quartz plates, lain on top of a sheet of paper with the alchemical symbol brimstone printed onto the page, indicating the colour and transparency of the films. See the supporting information, Section VII., for the associated Tauc plots that give the polymer bandgaps.

DIB and DVB polymers showed no absorbance at wavelengths longer than 850 nm, and very minor absorbance at 785 nm (0.0015 for DVB50-S50 and 0.0018 for DIB50-S50), suggesting they would only poorly absorb that excitation laser wavelength. Since fluorescence was observed during 785 nm Raman analysis, it may be that these polymers are exceptionally efficient at fluorescence, and this small absorption is sufficient to induce fluorescence capable of swamping out the weaker Raman signal. The UV/Vis data in the table of Figure 3 suggests that these polymers do not absorb at 1064 nm, and this excitation laser would not suffer from fluorescence.

DCPD polymers showed absorbances at wavelengths as long as 1072 nm, explaining their deeper brown colour. Qualitatively, the thin films of DCPD synthesized at 135 °C and 160 °C appear very similar in their profiles, but the films synthesized at the lower temperature have much more significant absorbance at longer wavelengths. Similarly, squalene polymers also

showed absorbance at longer wavelengths, though not with any great efficiency at wavelengths longer than 1000 nm. In general, the UV/Vis spectra suggest that DCPD and squalene polymers would absorb 785 nm laser light, giving rise to fluorescence in the Raman spectrum, and would also absorb 1064 nm light to some degree, suggesting that fluoresce may be possible at this wavelength. Therefore, it is expected that DCPD and squalene polymers may be harder to analyse by 1064 nm Raman spectroscopy than DVB or DIB polymers.



Figure S14: UV/Vis spectra of A) DVB, B) DIB, C) DCPD, and D) Squalene inverse vulcanised polymers. The first number in the naming convention is the weight percentage of crosslinker used in the reaction, the second number is the weight percentage of sulfur used in the reaction, and the third number, where present, is the reaction temperature in °C, where two different reaction temperatures were used.

Interestingly, these polymers, even in the form of tens of micrometre thick films, showed tremendous absorbances in the near UV (below 500 nm to the spectrometer limit of 300 nm), suggesting that these polymers could find applications as UV blocking materials, though the degradation seen in the attempts at UV Raman, detailed later on, would need to be studied first.

Using these UV/Vis spectra, the fluorescence spectra of the polymers were obtained at several excitation wavelengths of interest (see the supporting information, Section VIII.). Unfortunately, the limitations of the equipment prevented studies of the fluorescence under 1064 nm excitation light, but the fluorescence was measured under excitation wavelengths of 784 nm, 532 nm, 266 nm and any others where polymers showed peaks or shoulder peaks in their UV/Vis spectra. In brief, the polymers fluoresced at all wavelengths with which they were irradiated. When irradiated with shorter wavelength light, the fluorescent signals were of greater intensity; extremely intense with UV irradiation and very weak with 784 nm irradiation. This further confirms that fluorescence is an obstacle to Raman spectroscopy with conventional excitation lasers, but also suggests that polymer analyses by Raman spectroscopy should be carried out in the dark. This is because the polymers fluoresced at wavelengths far from the excitation laser wavelength, suggesting that stray light, could cause fluorescence that would interfere with Raman signal acquisition. The polymers also showed degradation under deep UV irradiation (266 nm). See the supporting information, Section VIII. for a more detailed discussion of the fluorescence data.



Figure S15: Tauc plot for DVB inverse vulcanised polymers.



Figure S16: Tauc plot for DIB inverse vulcanised polymers.



Figure S17: Tauc plot for DCPD inverse vulcanised polymers synthesized at 135 °C.



Figure S18: Tauc plot for DCPD inverse vulcanised polymers synthesized at 160 °C.



Figure S19: Tauc plot for squalene inverse vulcanised polymers.

#### VIII. Absorbance and Fluorescence Spectra of the Polymer Thin Films

The fluorescence spectra were obtained on the same thin films used for the UV/Vis spectrometry. Whereas taking into account the film thickness when comparing the UV/Vis data was simple, for the fluorescence spectrometry such a comparison may be less appropriate. This is because the optimum alignment for each sample cannot be taken into account. Samples were placed into the spectrometer and aligned such that they gave the maximum possible signal. However, this cannot take into account the spot size of the beam on each sample, which may have been different for each set up, skewing any comparison of the results between different samples. It should still be appropriate to compare the intensities of the spectra obtained for the same sample, at different excitation wavelengths, because the alignment of the system was not changed if the sample itself was not changed. In contrast, when comparing the intensities of two different samples' spectra, caution should be taken. Note that the samples did not degrade at any of the tested excitation wavelengths, except 266 nm, thereafter which, the polymer films appeared greyed where they had been irradiated. The 266 nm excitation wavelength spectra were always obtained last, to avoid any potential effects of sample degradation upon other excitation spectra. 266 nm excitation spectra were obtained as quickly as possible, using only one scan, in the hopes of obtaining the polymers' spectra and not the spectra of the degradation products, though again, caution should be exercised when observing these spectra. Besides this, all spectra were averaged over five scans, with emission and detection bandwidths of 2.5 nm, and a dwell time of 0.2 s, with the exception of 784 nm excitation spectra which needed longer dwell times of 1 s. These factors have been taken into account in the intensity scales of Figures S20 to S24, so accepting the potential issue of the alignment, all spectra should be comparable to one another.



**Figure S20**: Fluorescence emission scans at different excitation wavelengths for different DVB inverse vulcanised polymers.



**Figure S21**: Fluorescence emission scans at different excitation wavelengths for different DIB inverse vulcanised polymers.



**Figure S22**: Fluorescence emission scans at different excitation wavelengths for different DCPD inverse vulcanised polymers, which were synthesized at 135 °C.



**Figure S23**: Fluorescence emission scans at different excitation wavelengths for different DCPD inverse vulcanised polymers, which were synthesized at 160 °C.



Figure S24: Fluorescence emission scans at different excitation wavelengths for different squalene inverse vulcanised polymers.

Under 784 nm irradiation, all the polymers gave poor signals that became increasingly weak at emission wavelengths that were further from the excitation wavelength. With 784 nm excitation, the polymers showed nothing more than the background signal at emission wavelengths longer than 850 nm. The polymers showed a shoulder peak at about 825 nm emission. In all cases where 784 nm excitation was applied, the emission intensity was greater at wavelengths closest to the excitation wavelength, which is unfortunate, because this is where the Raman signal occurs in Raman spectroscopy. Even though the fluorescence from the polymers is weak with 784 nm excitation, because it occurs close to the excitation wavelength, it is still capable of obscuring the Raman spectrum, which is itself, a weak signal. This then illustrates why no Raman signal could be obtained with a 784 nm excitation laser. Between all the polymers excited with 784 nm light, it does not seem as though there is a consistent trend between the sulfur content and the fluorescence intensity, though this could be due to the aforementioned issue with the system alignment. Comparing between the polymers, it appears that polymers of DVB and DIB are the most efficient at fluorescing at 784 nm excitation, potentially due to contributions from their aromatic components. Interestingly, DCPD polymers reacted at 160 °C seem to be less effective at fluorescence than those reacted at 135 °C, suggesting that a more complete reaction may reduce the propensity to fluoresce.

The emission of fluorescence under 532 nm excitation often gave fluorescent signals with what appears to be a Raman signal overlapping with it. It appears that when the polymer contains an aromatic unit (DIB or DVB), the fluorescence is most intense with a high loading of crosslinker, and is least intense with a low loading of crosslinker. For the other crosslinkers used, it seems that the opposite is true; fluorescence is most intense with a high loading of crosslinker. Just like when under 784 nm excitation, DIB and DVB polymers gave more intense fluorescence than DCPD or squalene polymers when under 532 nm excitation. Again, it must be remembered that these results could be skewed by the different alignments used between the different polymers. Fluorescence stemming from 532 nm irradiation usually appeared as a decay in intensity, followed by a rise in intensity in the form of a broad peak. However, this broad peak was not always present, and even when it was, it usually had several smaller peaks super imposed upon it. For DVB's 532 nm excitation fluorescence spectra, DVB30-S70 showed essentially no broad peak, revealing several smaller peaks that are likely to be Raman signals. Interestingly, in the spectrum of DVB70-S30, despite the broad peak, one can see overlapping signals that roughly align with the supposed Raman spectrum seen in DVB30-S70's fluorescence spectrum. There are several other cases of this between the different polymer samples, but there appears to be no clear way to predict the appearance of these Raman signals. In contrast to the aforementioned failure of 532 nm Raman spectroscopy to acquire a Raman signal through the fluorescence, this data might suggest that obtaining a Raman spectrum with a 532 nm laser could be possible where inverse vulcanised polymers are concerned. However, there is a crucial flaw: under 532 nm excitation, the sulfur - sulfur band region would be expected to occur at wavelength between 544 nm and 547 nm, and comparing this wavelength range to the fluorescence spectra, it is obvious that no such signal ever appears with any clarity. Thus it can be concluded that analysis of the sulfur – sulfur band would not be possible with a 532 nm excitation laser, as the signal would always be eclipsed by fluorescence.

The 266 nm excitation spectra are somewhat more dubious to analyse because the polymer films degraded under UV irradiation, so it is hard to know what is the fluorescence of the polymer, and what is the fluorescence of the degradation products. Further confusing would be the attenuation of signal intensities as the polymers became increasingly degraded under the progressively increasing exposure times. Regardless, it is safe to say that no sulfur - sulfur Raman band will be observed in these fluorescence spectra, as this region would be expected to occur at 269 nm when under 266 nm excitation, and the fluorescence spectra were all obtained starting from 275 nm to ensure the photo multiplier tube detector was not over exposed and damaged during the experiment. In general, all 266 nm excitation spectra were more intense than spectra obtained with longer wavelength excitation. All the polymers' spectra appeared fairly similar, with a smaller peak centred at 300 nm, a larger peak centred at around 410 nm, and then a broad shoulder peak at around 480 nm. The data acquired at longer emission wavelengths should be treated with the most scepticism, as it is at these wavelengths where the polymer would have been exposed to 266 nm excitation for the longest and therefore would have been the most degraded. Once again, the polymers show no consistent pattern of fluorescence intensity with sulfur loading, and under this excitation wavelength, the polymers of different crosslinkers did not show much difference in their fluorescence intensities: no crosslinker gave a polymer that was particularly more efficient at fluorescence than another. Analogous to the 532 nm excitation spectra, there are several cases in the 266 nm excitation where weak peaks appear that could be Raman signals. Particularly peaks appear at 327 nm and 349 nm quite consistently between different spectra. It is plausible to consider that the broad peak at 300 nm could also be a Raman signal, but it is difficult prove whether this is true. For 266 nm excitation, it is important to note that the polymers gave nominal signals all across the measured range. This is in fact true for 532 nm excitation as well, though with weaker intensity. The only time the signal ever fell to background levels, was with 784 nm excitation at emission wavelengths longer than 850 nm. This implies that if one was measuring a Raman spectrum using 532 nm excitation, but the polymer was also exposed to other wavelengths of light, these could additionally cause fluorescence. Therefore, it can be concluded that elimination of background light would be beneficial not only for ambient light background reduction in Raman spectroscopy, but also

the elimination of additional fluorescence. This may be a particularly important consideration for 1064 nm Raman spectroscopy, which would not be expected to incite fluorescence on its own, but could be affected by fluorescent transitions induced by shorter wavelengths of light from ambient sources. That is, the polymers may have the potential to absorb wavelengths of light shorter than 1064 nm, and then fluoresce at wavelengths longer than 1064 nm, thereby obscuring the Raman signal.

#### IX. Screening of Different Raman Spectroscopic Techniques

1064 nm Raman spectroscopy is very similar to conventional Raman spectroscopy, with the exception that it uses the less widespread option of a 1064 nm excitation laser. This laser wavelength is usually too low energy to excite an electronic transition, thereby preventing fluorescence. Also a result of the low laser energy, laser burn is uncommon. Unfortunately, the Raman cross section is dependent on  $\lambda_{\text{excite}}^{-4}$ , where  $\lambda_{\text{excite}}$  is the wavelength of the excitation laser.<sup>3</sup> From this dependency it can be shown that when using a 1064 nm laser, the same signal will fall to 30 % of the intensity it would show when using a 784 nm excitation laser, limiting 1064 nm Raman spectroscopy to samples that are strongly Raman active. Since inverse vulcanised polymers contain a high density of highly Raman active modes, it was predicted that 1064 nm Raman spectroscopy would be capable of providing interpretable signals, and indeed 1064 nm Raman using a handheld instrument was successful in most cases at providing Raman spectra of polymer samples. DVB polymer blocks all gave spectra with the least baseline interference, showing identifiable bands all across the spectral range. DIB also gave interpretable spectra but were more difficult to acquire, and had more substantial baselines. DCPD and squalene showed very substantial baselines that heavily obscured most of the signals, which falls in line with the results of the UV/Vis spectroscopy that indicated these polymers had more substantial absorbances at longer wavelengths. Importantly, it was quite difficult to damage the polymer samples with 1064 nm laser irradiation, a stark advantage over several techniques soon to be discussed.

Fourier transform Raman spectroscopy can largely be considered as an extension of 1064 nm Raman spectroscopy, as they both use the same laser wavelength. However, Fourier transform Raman spectroscopy uses the addition of a Michelson interferometer to allow multiplexing measurements to bring several further advantages, such as shorter acquisition times which minimises the chance of laser burn, better resolution as there are no resolution limiting thin apertures, and an improvement in the background of the signal.<sup>3</sup> Samples for Fourier transform Raman spectroscopy were prepared with a hand operated press for preparation of KBr pellets. The well of the 7 mm pellet die was filled with a desired polymer powder with the excess powder being removed. The die set was placed in the hand operated press and the handle was squeezed and held for 15 seconds. The pellet was formed in the center of the die. The die with the pellet was then placed in the probe laser beam chamber of the FT-Raman spectrometer (Bruker Vertex 70 with a 70 a RAM II FT-Raman module). The FT-Raman operated with a Nd-YAG laser of wavelength 1064 nm and a spectral range from 50 to 3600 cm<sup>-1</sup> with resolution better than 0.4 cm<sup>-1</sup>. Spectra were averaged over 100 scans (130s total acquisition time) with a laser power between 1 and 100mW obtaining an excellent rejection ratio. Similar to 1064 nm Raman spectroscopy, Fourier transform Raman spectroscopy was successful in providing spectra of the polymers, with the same observations that DVB and DIB polymer spectra were easier to obtain than DCPD or squalene spectra.



Figure S25: Fourier Transform Raman spectra of DVB inverse vulcanised polymers.



Figure S26: Fourier Transform Raman spectra of DIB inverse vulcanised polymers.



Figure S27: Fourier Transform Raman spectra of DCPD inverse vulcanised polymers.



Figure S28: Fourier Transform Raman spectra of squalene inverse vulcanised polymers.

UV Raman spectroscopy is also similar to conventional Raman spectroscopy, with the exception that it uses UV wavelengths to excite Raman transitions. This seems counterintuitive, as a shorter laser wavelength will promote auto-fluorescent transitions that would obscure the Raman spectrum. However, even though the laser does promote auto-fluorescence, the energy of the laser shifts the fluorescence to much higher Raman shifts, leaving the lower end of the Raman spectrum free of a fluorescent background. This is because most fluorescent transitions occur at wavelengths longer than 300 nm, which when placed in comparison with a 266 nm excitation laser, equates to a Raman shift of about 4260 cm<sup>-1</sup>. Very few Raman modes occur at such high shifts, and so the spectrum is left free of fluorescence. An additional advantage of UV Raman is that since the Raman cross section is dependent on  $\lambda_{\text{excite}}^{-4}$ , a 266 nm excitation laser gives a signal approximately 75 times stronger than that given by a 784 nm excitation laser.<sup>3</sup> However, the shorter laser wavelength of UV Raman spectroscopy promotes laser burn, as it imparts a high amount of thermal energy to the sample, but also carries sufficiently energetic photons to allow photochemical reactions. This proved to be prohibitive to the analysis of inverse vulcanised polymers in UV Raman, as the polymers rapidly degraded and decomposed. Though the spectra showed no signs of fluorescence, they rapidly changed with the duration of laser exposure and therefore the degree of degradation, regardless of methodological optimisations. Thus, UV Raman is not suitable for the analysis of inverse vulcanised polymers and perhaps indicates that these polymers can be sensitive to UV light. Therefore, inverse vulcanised polymers should be stored in the absence of UV light, and possibly in total darkness. Further studies into the degradation of inverse vulcanised polymers in relation to their storage conditions is a research avenue that should receive attention in the future. Given that UV Raman spectroscopy was successful in avoiding the fluorescence of the polymers, further attention was paid to the excitation wavelength itself. Whether there was an excitation wavelength at the fringe of visible light and UV light that could avoid auto-fluorescence, without degrading the polymers before a signal can be obtained, was investigated. 366 nm light again, rapidly induced sample degradation, so alongside 266 nm Raman spectroscopy, it is not suitable. On the other hand, a 488 nm laser did show promise. Most samples gave good Raman signals with different sulfur related bands, however not all were free of fluorescence and careful method optimisation was necessary to manage laser absorption and heating damage.

Kerr gated Raman spectroscopy is an advanced Raman spectroscopic technique that allows the separation of Raman signals and fluorescent signals based on the time lag between their emissions. Because Raman scatter occurs through an intermediate virtual state, relaxation from this virtual state is essentially instantaneous. Fluorescence on the other hand, occurs through an intermediate real state. Because the molecule is excited to a real state, it spends a finite amount of time in that state before relaxing and emitting a fluorescent photon. Thus, fluorescent signals are emitted a short amount of time after a Raman signal. Kerr gated Raman spectroscopy uses this short time delay to separate the Raman signal from the fluorescent signal, thereby eliminating fluorescent backgrounds.<sup>4</sup> However, Kerr gated Raman spectroscopy is not a widespread technique, and so it is unlikely it will see significant uptake in the field of inverse vulcanised polymers; the analysis performed here was done as a proof of concept. Kerr gated Raman spectroscopy was successful in obtaining polymer spectra for all samples, even the ones where other techniques struggled due to fluorescence. Though the signals are weaker, Kerr gated Raman spectroscopy could be a useful last resort where other techniques fail. The method for preparing samples for Kerr-gated Raman spectroscopy was the same as the method for Fourier transform Raman Spectroscopy.



Figure S29: Kerr gated Raman spectra of DVB inverse vulcanised polymers.



Figure S30: Kerr gated Raman spectra of DIB inverse vulcanised polymers.



Figure S31: Kerr gated Raman spectra of DCPD inverse vulcanised polymers synthesized at 135 °C.



Figure S32: Kerr gated Raman spectra of DCPD inverse vulcanised polymers synthesized at 160 °C.

#### X. Evidence of Oxidation of Inverse Vulcanised Polymers

DVB polymers provided clear spectra, even without method optimisation, so they were useful candidates for simplistic initial analyses. One such analysis was that, in the 1064 nm Raman spectra, there appeared to be evidence of sulfonic acids and sulfones  $(1025 - 1060 \text{ cm}^{-1} \text{ and } 1050 - 1210 \text{ cm}^{-1}$  respectively). If these moieties are present in the structures of inverse vulcanised polymers, then it suggests that oxidation may play a role in the polymerisation process. This conclusion and the assignments themselves were difficult to confirm on their own, so to confirm the presence of oxidised sulfur, the syntheses of DVB30-S70, DVB50-S50 and DVB70-S30 were repeated, but this time an inert atmosphere of nitrogen was maintained throughout the polymerisation and curing processes (the polymers had to be cured upon the hotplate rather than in the oven). Due to the affixed septum and gas balloon on the reaction vial, and the curing upon the hotplate which has been shown to give different results to oven curing previously, these new polymers: DVB30-S70-N2, DVB50-S50-N2 and DVB70-S30-N2, were not directly comparable to the previous ones. Therefore, a second batch of polymers were synthesized in the same way as DVB $\alpha$ -S $\beta$ -N2, but this time, the balloons and reaction vials were filled with air instead of nitrogen, giving DVB30-S70-Air, DVB50-S50- Air and DVB70-S30-Air.



**Figure S33**: Raman spectra, obtained on a handheld instrument, of DVB polymers synthesized under air and nitrogen atmospheres, A) before spectral processing, and B) after spectral processing.

All of the reactions for DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air took longer than their unsealed reaction vial counterparts: DVB $\alpha$ -S $\beta$ . This is likely because the presence of the septum prevented the loss of volatilised DVB. It has been shown previously that the greater the quantity of crosslinker in comparison to sulfur, the slower the reaction proceeds; likely due to the decreased proportional presence of initiating sulfur radicals.<sup>5</sup> Therefore, if DVB evaporates over the course of the reaction, as it has been proven to do previously, the proportion of sulfur in the reaction is raised, leading to a faster rate.<sup>5</sup> Sealing the reaction vial would prevent the loss of DVB and therefore keep the proportion of sulfur lower than if the septum was absent, thereby decreasing the reaction rate. The conclusion that the loss of DVB is prevented by the fixture of a septum is supported by the CHNS data for DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air, where the percentage of sulfur is lower and the percentage of carbon and hydrogen is higher than those values for DVB $\alpha$ -S $\beta$ . In fact, the CHNS data for DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air mirror their

predicted values very closely (Table S2), unlike DVB $\alpha$ -S $\beta$ , which show significant evidence of crosslinker evaporation. It should be no surprise then, that with such different sulfur compositions between DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air compared to DVB $\alpha$ -S $\beta$ , that their glass transition temperatures are also very different.

Polymer	DVB30- S70-N2	DVB30- S70-Air	DVB50- S50-N2	DVB50- S50-Air	DVB70- S30-N2	DVB70- S30-Air
C expected (%)	27.68	27.68	46.13	46.13	64.58	64.58
C actual (%)	22.66	26.69	44.85	43.93	58.96	62.80
H expected (%)	2.32	2.32	3.87	3.87	5.42	5.42
H actual (%)	1.51	2.11	3.70	3.64	4.92	5.31
S expected (%)	70.00	70.00	50.00	50.00	30.00	30.00
S actual (%)	71.97	70.40	51.92	52.53	36.02	30.72
Glass transition temperature from DSC / °C	52.89	55.08	99.27	100.81	79.60	87.88

Table S2: Analyses of inverse vulcanised polymers synthesized under air or nitrogen

The data in Table S2 indicates that DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air are indeed different, though this difference is quite small between DVB50-S50-N2 and DVB50-S50-Air, wherein the CHNS data values are all within a percent of each other, and the glass transition temperatures are very close. For the other four polymers, the differences are pronounced. The glass transition temperature is lower when the reaction was done under nitrogen, and the CHNS values differ by some margin. For DVB30-S70-N2 and DVB70-S30-N2, the %C and %H values are lower than the expected values, whilst the %S value is higher than expected. Contrastingly, DVB30-S70-Air and DVB70-S30-Air adhere much more closely to their expected values, and therefore, their %C and %H values are higher, and their %S values are lower, than their under-nitrogen counterparts. Though it seems that the atmosphere the reaction is performed under affects the resulting polymers, the reasons for these differences cannot be determined here. It was supposed that the DVB $\alpha$ -S $\beta$ -Air polymers may have incorporated some oxygen atoms into their structure, and that any leftover unaccounted-for mass in the CHNS analysis may be due to oxygen. If this was the case, then the unaccounted-for mass should be higher in the DVB $\alpha$ -S $\beta$ -Air polymers compared to DVB $\alpha$ -S $\beta$ -N2, however this was not consistently the case in the data of Table S2.

Regardless, the reactions of DVB $\alpha$ -S $\beta$ -N2 took longer than the analogous DVB $\alpha$ -S $\beta$ -Air reaction, suggesting that oxidation does play some role in the reaction mechanism. Furthermore, as depicted in Figure S34, the DVB $\alpha$ -S $\beta$ -N2 polymers are visually different to their DVB $\alpha$ -S $\beta$ -Air counterparts, being slightly lighter and more yellow in colour. Unfortunately, 1064 nm Raman spectroscopy could not identify a significant difference between DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air, as their spectra appeared the same (Figure S33). The peaks that were initially assigned to sulfonic acids and sulfones appeared in both DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air spectra, suggesting these peaks are not related to oxidation products, or that somehow sulfonic acids and sulfones are forming despite the exclusion of oxygen from the reaction; a conclusion that seems highly unlikely. Regardless, even though Raman spectroscopy could not distinguish the polymers formed under nitrogen and under air, the other characterisations suggest that the role of oxidation in the mechanism of inverse vulcanisation merits more dedicated studies.



Figure S34: A photograph that shows the visual differences between the DVB $\alpha$ -S $\beta$ -N2 and DVB $\alpha$ -S $\beta$ -Air polymers.

## XI. DSC Thermograms for the Second Batch of Polymers



Figure S35: DSC thermograms of the second batch of DVB inverse vulcanised polymers.



Figure S36: DSC thermograms of the second batch of DIB inverse vulcanised polymers.



Figure S37: DSC thermograms of the second batch of DCPD inverse vulcanised polymers.



Figure S38: DSC thermograms of the second batch of squalene inverse vulcanised polymers.

## XII. 1064 nm SERS Spectra for DVB Polymers



Figure S39: 1064 nm Raman spectra of DVB polymers, with and without gold nanorods on their surface.

#### XIII. Density Functional Theory Calculation Method

To identify a suitable method of predicting Raman spectra, the experimental 1064 nm Raman spectra of six model molecules were obtained: dimethyldisulfide, dimethyltrisulfide, diallyldisulfide, diallyltrisulfide, diphenyldisulfide, and dibenzyldisulfide; all containing a sulfur – sulfur bond. Next, the Raman spectra of these molecules were predicted using density functional theory in the Gaussian 09 code, using different density functionals with the def2-TZVPP basis set. All spectra were calculated assuming 1064 nm excitation at 298.15 K, in the gas state in a vacuum, after an initial energy minimization using MMFF molecular mechanics. The four functionals tested were, BP86, HSE06,  $\omega$ B97XD, and M062X, (all used in conjunction with the def2-TZVPP basis set, with and without Gimme's B3(BJ) empirical dispersion correction) as it was thought that these functionals would provide a good spread of functionals at different levels of theory: for example  $\omega$ B97XD is a range separated hybrid generalised gradient approximation functional, whereas M062X is a global hybrid meta generalised gradient approximation. B3LYP and EDF2 were also preliminarily tested with a variety of basis sets, but although EDF2 was better than B3LYP, both were quite poor at replicating the Raman spectra. The predicted Raman spectra from these calculations, were then compared to the experimental Raman spectra, and it was found that the spectra calculated by an initial energy minimisation with MMFF molecular mechanics, followed by geometry optimisation and energy calculation with the BP86 functional and the def2-TZVPP basis, with a D3(BJ) empirical dispersion correction, gave the best fit to the experimental data. Grimme et al. singled out a charged sulphur ring system,  $S_8^{2+}$ , as having sulfur - sulfur bonds elongated by DFT-D3, which are then corrected with DFT-D3(BJ) which may explain why this empirical dispersion was advantageous in this case.<sup>6</sup> See below for the comparison of the experimental and calculated spectra. To further improve the fit of the predicted Raman spectra to the experimental Raman spectra, parameterisation can be carried out, which would entail using the experimental peak data to correct the predicted data, which is detailed in section XV. Figures S40 to S50 all show predicted Raman spectra which were predicted by the optimised method mentioned above (geometry optimisation and energy calculation using BP86+D3(BJ)/def2-TZVPP). For the model compounds, energy minimisation with MMFF molecular mechanics was used before geometry optimisation. For the polymer models, a conformer search was performed instead of energy minimisation, which was also done using MMFF molecular mechanics.



**Figure S40**: Comparison of the experimental and predicted Raman spectra for dimethyldisulfide, as well as a geometry optimised structure for dimethyldisulfide.



**Figure S41**: Comparison of the experimental and predicted Raman spectra for dimethyltrisulfide, as well as a geometry optimised structure for dimethyltrisulfide.



**Figure S42**: Comparison of the experimental and predicted Raman spectra for diallyldisulfide, as well as a geometry optimised structure for diallyldisulfide.





**Figure S43**: Comparison of the experimental and predicted Raman spectra for diallyltrisulfide, as well as a geometry optimised structure for diallyltrisulfide.

**Figure S44**: Comparison of the experimental and predicted Raman spectra for diphenyldisulfide, as well as a geometry optimised structure for diphenyldisulfide.



**Figure S45**: Comparison of the experimental and predicted Raman spectra for dibenzyldisulfide, as well as a geometry optimised structure for dibenzyldisulfide.

## XIV. Additional Calculated Data for the Polymer Models



Figure S46: Predicted Raman spectra for the lowest energy conformer of the rank 2 polymer model.



Figure S47: Predicted Raman spectra for the lowest energy conformer of the rank 3 polymer model.



Figure S48: Predicted Raman spectra for the lowest energy conformer of the rank 4 polymer model.



Figure S49: Predicted Raman spectra for the lowest energy conformer of the rank 5 polymer model.



Figure S50: Predicted Raman spectra for the lowest energy conformer of the rank 6 polymer model.

**Table S3**: Selected predicted Raman data for the lowest energy conformers of the polymer models. The column "S-S mode" indicates whether the vibrational mode had a major, minor, or no contribution from the stretching of S-S bonds. Other information such as the reduced mass, force constants of vibration, and IR intensities were also calculated, but there was too much information to represent here. All data presented here is parameterised by the method shown in section XV.

Rank 2 Cis RR			Ran	nk 2 Cis RS	5	Rank 2 Trans RR			Rank 2 Trans RS		
Harmonic	Scattering	S-S									
Frequency /	Activity /	mode									
cm-1	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm-1	A <sup>4</sup> AMU <sup>-1</sup>	
411.7734	43.9584	minor	412.0934	10.7514	none	411.6211	4.4105	minor	411.6569	23.5847	none
411.8257	2.0198	none	416.7281	35.3509	minor	411.9498	24.6653	none	416.8122	22.2078	minor
453.0468	9.5576	none	458.1715	50.6971	none	427.2881	433.0026	major	427.9433	525.1084	major
467.3877	106.3597	major	468.9694	52.4176	major	461.8773	64.9921	major	465.5752	23.6512	major
501.5938	8.5828	major	504.2803	41.3131	major	501.6190	10.7452	major	503.4717	66.5205	major
514.0890	2.0881	none	515.2230	145.4141	major	514.3027	4.4215	minor	518.5418	25.3761	major
518.0579	196.4125	major	519.3268	32.4095	major	522.9172	15.9142	major	523.8794	43.2095	major
526.0024	38.3230	major	545.2028	20.9916	major	528.9543	38.1197	major	545.7305	20.5165	major
584.7102	331.2205	minor	593.1634	112.4294	none	592.8815	104.0275	minor	597.1947	4.3139	minor
593.6597	1.0985	none	597.6316	23.3111	minor	596.7208	1.2198	minor	600.5305	22.2521	none
597.5700	0.5593	none	600.5625	8.3876	minor	598.5526	37.4985	minor	615.0292	49.3528	minor
601.2379	22.5452	minor	615.7314	55.7008	major	626.0925	35.0898	none	625.9299	34.4288	minor
633.2633	21.7490	minor	633.6964	13.4976	none	633.6927	15.7119	minor	638.7836	22.7698	minor
634.0075	10.0244	none	639.4643	24.6703	minor	651.7991	154.9510	none	651.4549	164.4431	none
Rank 3 Cis RR		ł	Rar	k 3 Cis RS	;	Rank 3 Trans RR			Rank	3 Trans F	s
Harmonic	Scattering	S-S									
Frequency /	Activity /	mode									
cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>	
412.9754	26.4742	minor	412.5632	10.3926	none	411.3822	4.9254	none	412.8191	9.6051	none
414.4342	201.4113	major	412.9396	22.8359	minor	413.6430	7.2847	none	412.8228	18.6359	none
416.5072	75.3334	major	414.4569	5.0878	none	418.7601	1.0022	major	415.7163	333.5915	none
440.9122	16.6726	major	423.4074	298.2862	major	431.0992	688.3502	major	423.1557	0.0000	major
458.4569	133.1522	major	451.4734	178.2511	major	442.8158	137.5243	major	452.2184	0.0000	major
468.1230	113.7389	major	454.1852	180.2667	major	460.1553	186.8184	major	454.0759	493.8708	major
491.7709	313.4010	major	485.1958	166.1340	major	490.8514	14.7567	major	485.6527	0.0578	major
494.2200	60.8271	major	486.3448	774.9285	major	493.4904	116.6251	major	485.7327	1012.1359	major
511.4937	9.7329	major	520.1372	2.7627	major	518.6202	5.4620	minor	521.2547	8.7433	major
526.8940	8.0678	major	524.9213	6.8473	minor	524.0272	6.2375	major	524.1209	0.0000	minor
587.7828	18.2086	major	571.0755	4.8702	major	594.8395	4.1406	none	573.2558	7.5660	major

600.1860	0.9246	minor	578.4125	3.4578	minor	598.9612	1.8490	none	577.0973	0.0000	minor
605.1864	54.0447	minor	629.7741	11.1729	minor	622.4858	4.0897	none	629.8583	36.6638	minor
626.3447	17.6553	none	630.0651	23.0534	minor	624.8618	63.3734	none	630.0056	0.0000	none
633.3035	14.2132	minor	674.4097	18.5564	minor	641.2799	43.5275	none	675.6216	75.8417	none
Dave			Dave			David	4 T		Daul	4 T	<u>.</u>
кап 🛛	K 4 CIS KR		кап	ik 4 CIS KS	)	капк	4 Trans R	K	капк	4 Trans F	(5
Harmonic	Scattering	S-S									
Frequency /	Activity /	mode									
cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>	
400.6803	642,2028	maior	390.3287	957.3765	maior	400.3761	771,2256	maior	392,7018	881,4957	maior
407 6425	499 5324	major	396 2331	537 9756	major	403 1937	266 9065	major	393 7457	722 2565	major
407.0423	0 0523	minor	/12 2087	11 1942	minor	405.1557	23 7250	none	/12 3531	8 4828	minor
412.5142	17 550	minor	412.2367	26 2520	nono	411.7033	23.7250	minor	412.3331	22 2709	nono
412.3209	17.5550	major	412.7735	20.3330	maior	411.5510	126 8027	major	412.0331	122,5706	none
425.4762	40.5201	major	425.7205	197.9591	major	421.0099	120.8027	major	424.9371	152.6227	major
428.8168	133.9240	major	470.8503	184.1833	major	441.3028	192.3077	major	470.3225	245.7526	major
483.2879	311.8079	major	492.5069	226.9084	major	483.7930	331.6759	major	493.7417	62.6067	major
489.9997	516.2813	major	494.4958	135.4193	major	494.7279	103.1188	major	494.4201	384.1114	major
496.6323	39.1351	major	495.3695	158.7929	major	498.2750	60.3811	major	495.8000	36.3398	major
504.1808	84.4471	major	496.6383	52.0667	major	502.5217	92.5810	major	496.4060	63.1493	major
520.0964	17.5263	minor	516.5078	17.4876	major	515.6426	33.5877	major	515.9025	18.3531	major
521.9684	8.1905	minor	519.8395	5.1685	major	522.1842	7.2875	minor	519.8807	4.9380	major
573.5941	3.3817	minor	575.7124	3.1759	minor	579.5541	2.2715	major	575.2487	2.9023	minor
596.3330	1.9188	minor	593.6194	51.4838	minor	596.5942	2.4242	minor	593.9669	44.6773	minor
622.2743	91.5249	minor	604.3517	120.0126	minor	622.2197	69.4148	minor	604.1034	110.2346	minor
630.2482	17.4985	none	630.1858	15.8992	none	631.1335	14.8694	none	630.1017	16.5747	none
642.6771	159,3102	minor	634,5308	22,6162	minor	643.0747	123,2114	none	634.3235	19,5151	minor
			-					-			
Ran	ik 5 Cis RR	ł –	Ran	ik 5 Cis RS		Rank	5 Trans R	R	Rank	5 Trans F	RS
Harmonic	Scattering	S-S									
Frequency /	Activity /	mode									
cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>		cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>	
388 1568	69 3209	maior	394 1591	36 1079	maior	391 2217	66 5261	maior	392 3218	73.0750	maior
389.0103	37 1931	major	399 2810	17 4536	major	391 3181	58 7818	major	397.4060	35 6586	major
401.0111	130 2631	major	411 2268	92.0815	none	409 7935	190 2111	minor	411 2103	59.0762	minor
401.0111	24 7200	nana	411.2200	42 5205	minor	409.7955	42 2004	minor	411.2195	1 7270	nano
411.9780	24.7390	none	411.5514	45.5595	minor	410.2988	42.3004	minor	415.2055	1.7279	none
415.4008	65./11/	minor	415.8521	26.2684	minor	415.0129	159.7793	minor	416.1299	315.3422	major
437.4134	105.1000	minor	416.9240	653.9449	minor	415.1684	1127.3358	minor	449.9798	424.1479	major
448.5759	109.6894	major	450.8695	187.1579	major	444.2874	76.5818	major	451.5963	392.1802	major
449.0347	408.1138	major	452.4054	458.5190	major	446.3756	771.6920	major	478.1962	135.2781	major
487.9784	892.9743	major	487.9527	47.7510	major	481.2111	676.5189	major	489.5003	52.6240	major
490.1415	102.7827	major	491.1670	215.6101	major	483.3188	36.8142	major	493.2318	160.2203	major
494.2409	167.9065	major	503.4716	159.7523	major	497.1290	35.3924	major	499.3454	144.9918	major
502.0843	92.5525	major	504.2261	42.2576	major	499.1148	138.1621	major	504.2910	242.4887	major
518.7504	26.3209	minor	523.5128	3.1610	major	510.8502	2.8844	major	506.0064	24.6927	major
536.3032	4,7866	minor	523.6828	23.3032	maior	511.6300	325,7249	maior	523.2622	13.0038	maior
569.8530	5,5194	minor	598,9516	4,2753	minor	597,5476	24,8637	minor	595.9073	127.6340	minor
578,4307	2,7840	minor	599.6623	3,7493	minor	597,5988	22,6105	minor	600.0327	3,2026	minor
629.8432	17.2945	none	624,1934	36,9757	none	611.5802	14,9546	none	600.8608	30.8049	minor
629 8927	18 3394	none	624 4123	50 3724	none	612 7275	77.0503	none	624 2077	43 0274	none
025.0527	-	none	6/0 /8/2	14 5168	none	633 7101	17.637	none	632 1357	17 20/1	none
-	-	-	650 1162	204.0096	nono	624 2602	17.4037	nono	640.0275	101 0175	nono
-	-	-	050.1102	204.0080	none	034.2033	43.0482	none	045.0275	101.8175	none
Ran	k 6 Cis RR	2	Ran	Rank 6 Cis RS   Rank (				R	Rank	: 6 Trans F	RS
Harmonic	Scattering	5-5	Harmonic	Scattering	5-5	Harmonic	Scattering	S-S	Harmonic	Scattering	5-5
Frequency /	Activity /	mode									
cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>	moue	cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>	moue	cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>	mode	cm <sup>-1</sup>	A <sup>4</sup> AMU <sup>-1</sup>	moue
413.0592	14 2040	none	/10 3790	18 08/3	minor	/13 1307	22 1460	minor			
412.0042	21 5052	minor	410.3750	11 4060	minor	413.1307	10 2962	minor			
415.9942	51.5955	minor	414.5565	206 2024	minor	413.9541	10.3803	minor			
425.2346	122.3130	major	419.9620	206.2834	minor	418.3518	70.9736	minor			
428.5001	225.8488	major	430.6481	162.9107	major	419.2801	370.1081	minor			
431.8919	114.5437	major	435.3812	238.0594	major	427.1293	182.7614	major			
434.2325	136.8524	minor	447.9821	1344.0407	major	427.2573	24.2178	major			
460.2109	92.2787	major	461.0972	93.5510	major	460.9669	111.3420	major			
461.1576	1761.1909	major	462.0913	671.4385	major	462.2308	1804.9350	major			
487.7357	609.5249	major	484.9899	73.7002	major	492.1536	25.5561	major	Failed due	to not enough mo	mony
490.3082	279.4929	major	487.3189	326.0917	major	492.2097	360.7760	major	raileu uue	to not enough me	погу
491.7993	40.8893	major	492.7225	400.7039	major	495.1332	337.3049	major			
495.0532	148.5259	major	495.0226	44.9482	major	496.4744	10.3105	major			
521.1494	20.0117	minor	501.6518	10.7311	maior	524.7595	3.6240	minor			
521,8646	12,4632	minor	526,9071	7,7061	minor	524,8410	19,1840	minor			
572,8259	3,4926	minor	575,4898	2,5421	minor	575,3645	4,8570	minor			
573 8661	3 4758	minor	575 9102	3 3632	minor	575 5665	2 0389	minor			
630 4014	21 6082	none	629 7701	2 0306	none	630 1318	2 6998	none			
630 7967	14 4030	none	630 9454	24 8881	none	630 7908	24 1895	none			

#### **XV.** Parameterisation of the Predicted Spectra

In terms of parameterising the Raman shifts, it was found that the best improvement in accuracy was given by simply adding 15 cm<sup>-1</sup> to the values, because on average the calculated spectra underestimated the Raman shifts of sulfur region modes by approximately 15 cm<sup>-1</sup>. Parameterisation of the intensities of the calculated spectra was a great deal more complicated than the Parameterisation of the Raman shifts, but was also more important. In general, the intensity of Raman modes is much more difficult than the peak Raman shifts to predict accurately through computational chemistry.

The first obstacle to parameterising the intensities was to overcome the fact that the experimental and calculated spectra of the standard molecules have different units that are not easily interchanged. An additional problem is that the experimental spectra are influenced by experimental parameters such as laser intensity and integration time, which the calculated spectra were not. To circumvent this problem, normalisation and a ratiometric approach was employed. Regardless of any parameters and units, the ratio of two different peak intensities should not vary. Because an aromatic mode at approximately 1600 cm<sup>-1</sup> exists within the spectra of the DVB polymers as well as two of the standard molecules, diphenyldisulfide and dibenzyldisulfide, the ratio of the intensity of the aromatic mode over the intensity of the sulfur modes could be used to apply the corrections. That is, the ratio in the experimental spectra could be used to correct that ratio from the calculated data. Since this correction centres around the aromatic mode, it was sensible to normalise the experimental and calculated spectra to their aromatic modes, thereby eliminating the issue of differing units. Observing the comparison of the experimental and calculated spectra of the standard molecules, and comparing the experimental DVB polymer spectra to the calculated polymer model spectra, it is clear that the calculated spectra consistently underestimate the intensities of the sulfur – sulfur modes in comparison to the aromatic modes. The next complication to the parameterisation was that the degree to which the sulfur modes were underestimated could be dependent on the Raman shift that the modes occurred at. As such, the parameterisation function had to vary with Raman shift, so that the parametrisation value could vary with the Raman shift. The best intensity parameterisation model was found to be a polynomial function as detailed in Figure S51. Note that the experimental intensity values have been baseline corrected, to eliminate the effects of non-Raman scatter effects, which was found to be crucial. The number of significant figures included in the intensity parameterisation was also found to be crucial. From this parameterisation model, the polymer model calculated spectra can be parametrised by multiplying the peak intensity of a Raman mode by the appropriate B/A value for that Raman shift.



**Figure S51**: Parameterisation model for the intensities of calculated Raman spectra. Black points are for dibenzyldisulfide, red points are for diphenylsulfide.

A = experimental intensity ratio = (experimental aromatic mode intensity  $(\sim 1600 \text{ cm}^{-1}))/(\text{experimental} \text{ mode of interest intensity})$ 

B = calculated intensity ratio = (calculated aromatic mode intensity (~1600 cm<sup>-1</sup>))/(calculated mode of interest intensity)

 $R^2 = 0.75$ 

## XVI. Step by Step Guide for the Quantification of Dark Sulfur by Raman Spectroscopy

- 1. Acquire a polymer spectrum and divide the intensity by the integration time.
- 2. Identify the elemental sulfur signal at 220 cm<sup>-1</sup> and then use a linear baseline correction to eliminate the contribution of the fluorescent background.
- 3. Acquire the spectrum of elemental sulfur using the same laser power as was used for the polymer; the integration time can be different in order to prevent issues with saturating the signal detector. Divide the intensity of this spectrum by the integration time.
- 4. Determine the mass percentage of sulfur in the polymer by another method, such as CHNS combustion microanalysis.
- 5. Multiply the elemental sulfur spectrum intensity by the determined mass percentage of sulfur over 100.
- 6. Calculate the following ratio: intensity of the 220 cm<sup>-1</sup> peak in the elemental sulfur spectrum ÷ intensity of the 220 cm<sup>-1</sup> peak in the polymer spectrum. Multiply the result by 100 to get the percentage of sulfur in the polymer that is not polymerised.

Even if the mass percentage of sulfur in the polymer cannot be obtained confidently, this method can still be used to qualitatively compare the content of elemental sulfur between different polymers. The aforementioned process should simply be carried out until the point at which the mass percentage of sulfur is needed. Instead of proceeding further, the signal intensity of the 220 cm<sup>-1</sup> peak can then be directly compared to the equivalent peak in other polymers. Note that in order for this qualitative method to be valid, all polymer spectra must be obtained at the same laser power, and then the intensities of the spectra must be corrected for any differences in integration time.

#### **XVII. Calculation of Expected Sulfur Rank**

If it is assumed that all double bonds react and that there are no sulfur loops in the polymer, then it can be deduced that the number of double bonds equals the number of sulfur bridges. This is because it does not actually matter how the sulfur bridges interconnect the organic units, the number of sulfur bridges is theoretically the same in every scenario. Figure S52 illustrates this conclusion.



Perfectly Branched (all crosslinkers are in the same environment, no cyclic systems anywhere in the structure)



Perfectly Crosslinked (maximum number of cyclic systems in the structure)



Figure S52: Schematic connectivity diagrams.

Inside every 'unit cell', regardless of the connectivity of the structure, there are two double bonds and four halves of a sulfur bridge. In other words, there is a one to one ratio of double bonds to sulfur bridges. Similar models can be generated for crosslinkers containing three, four, or more double bond sites. One way to rationalise the justification of why the connectivity does not affect the ratio of double bonds to sulfur bridges is to consider a large cyclic chain of sulfur atoms. This chain can be crosslinked by inserting a carbon skeleton with two double bonds. This would divide the cyclic sulfur chain into two sulfur bridges with two double bond sites inserted into it. If a second crosslinker is added, the sulfur chains are divided again to yield four sulfur bridges, with four double bond sites. Figure S53 illustrates how it does not matter where the crosslinkers are inserted; the result is always the same.



Figure S53: Crosslinking Diagram.

With this fact in mind, that for all ideal structures there is one sulfur bridge for every double bond, it is simple to calculate the average expected sulfur rank. The number of sulfur atoms should be calculated from the sulfur mass that was input into the polymer. The number of sulfur atoms constituting elemental sulfur (sulfur that is not part of the polymer network) should be deducted from this total. This number of sulfur atoms should then be divided by the number of double bonds that were successfully polymerised. This number of double bonds can be calculated if the molecular mass of the crosslinker, the number of double bonds in each molecule of crosslinker, and the mass of crosslinker that actually polymerised is known. The latter of these three can be determined from the elemental analysis by the following equation, rearranged for "mass of crosslinker":

$$\frac{Mass \ percentage \ of \ sulfur}{100} = \frac{input \ mass \ of \ sulfur}{input \ mass \ of \ sulfur \ + \ mass \ of \ crosslinker}$$

#### XVIII. Step by Step Guide for Determining the Sulfur Rank by Raman Spectroscopy

- 1. Acquire a polymer spectrum, and if it is present, integrate the 218 cm<sup>-1</sup> elemental sulfur band to find its intensity. This should be done by using a linear baseline to remove the fluorescent background.
- 2. Multiply the obtained area of the 218 cm<sup>-1</sup> peak by 0.0891 to find the area of the 434 cm<sup>-1</sup> elemental peak. The value of 0.0891 was determined from the intensity ratio of the 218 cm<sup>-1</sup> peak versus the 434 cm<sup>-1</sup> peak in a pure elemental sulfur spectrum.
- 3. Multiply the obtained area of the 218 cm<sup>-1</sup> peak by 0.7492 to find the area of the 474 cm<sup>-1</sup> elemental sulfur peak. The value of 0.7492 was determined from the intensity ratio of the 218 cm<sup>-1</sup> peak versus the 474 cm<sup>-1</sup> peak in a pure elemental sulfur spectrum.
- 4. Identify the upper and lower limits of the sulfur sulfur band in the polymer spectrum, which in this work, were usually around 350 cm<sup>-1</sup> and 550 cm<sup>-1</sup>.
- 5. Subtract a linear baseline from the sulfur sulfur band.
- 6. Perform band deconvolution on the sulfur sulfur band using the minimum number of bands, plus two peaks for elemental sulfur: one at 434 cm<sup>-1</sup> and one at 474 cm<sup>-1</sup>, the areas of which are now known from step two and three respectively. Typically, an error of  $\pm 1$  cm<sup>-1</sup> on the band centre of the 434 cm<sup>-1</sup> and the 474 cm<sup>-1</sup> peaks was permitted, and an error of  $\pm 10$  % in their areas was permitted.
- 7. Once band deconvolution gives rise to a good mathematical fit with the minimum number of Gaussian bands, note the area (the  $G_{n,real}$  value), band centre, and FWHM value of each deconvoluted band. Disregard the deconvoluted peaks for elemental sulfur.
- 8. Calculate a range of Raman shifts for each band, where the upper limit of the range is the band centre + (FWHM / 2), and the lower limit is the band centre (FWHM / 2). Label each range as Group n, so that each deconvoluted peak has its own distinct group. Note that if one group's band centre occurs within the range of another group, these two groups can be combined into a single group.
- 9. For sulfur rank 2, organise the computational data in Table S3 (which must first be parameterised) into the groups created in step eight, based on whether the calculated peak's band centre falls within the range of Raman shifts for that group. Where a calculated peak's band centre falls with 5 cm<sup>-1</sup> of a boundary between two groups, halve that peak's intensity and place it into both groups. Once this sorting process is complete, sum together the intensities contained within each group. This will yield the intensity that sulfur rank 2 provides to each group.
- 10. Repeat step 9 for each sulfur rank, thus obtaining a series of  $C_{n,m}$  values, where C is the summed in intensity of all computationally predicted peaks that occur within group n, for sulfur rank rm.
- 11. Assemble the following equation for each group:  $r_3C_{n,r3}$  $r_2C_{n,r_2}$ + $^+$  $r_4C_{n,r4}$ + $r_5C_{n,r5}$  $^+$  $r_6C_{n,r6}$ G<sub>n,real</sub> where G<sub>n,real</sub> is the intensity of the group from the experimental data (step 7), C<sub>n,rm</sub> is the intensity that sulfur rank m should contribute to group n (steps 9 and 10), and  $r_m$  are the proportional populations of sulfur ranks 2, 3, 4, 5, and 6 respectively. This should lead to several simultaneous equations, where the number of equations is equal to the number of groups. The  $r_m$  value for a given sulfur rank is the same in each equation.
- 12. Solve the simultaneous equations created in step 11 for preliminary  $r_m$  values. To simplify this process, one can consider  $r_5$  and  $r_6$  to be negligible, such that only three simultaneous equations need be solved. If the computational data used in this study were completely accurate, then these simultaneous equations would give accurate  $r_m$  values. Since this is not the case, they give preliminary  $r_m$  values that can be improved in the next step.
- 13. Assemble the following equation for each group  $r_2C_{n,r_2}$  $r_3C_{n,r_3}$  $r_4C_{n,r4}$ + $r_5C_{n,r_5}$ G<sub>n,predicted</sub> = + $r_6C_{n,r_6}$

where  $G_{n,predicted}$  is the intensity of the group calculated from the equation,  $C_{n,rm}$  is the intensity that sulfur rank m should contribute to group n (steps 9 and 10), and  $r_m$  are the proportional populations of sulfur ranks 2, 3, 4, 5, and 6 respectively. This should lead to several simultaneous equations, where the number of equations is equal to the number of groups. The  $r_m$  value for a given sulfur rank is the same in each equation.

- 14. Adjust the  $r_m$  values in a trial and error iterative fashion until the values for  $G_{n,predicted}$  are as close as possible to the corresponding  $G_{n,real}$  values. This process is complete when a minimum difference between the  $G_{n,real}$  values and the  $G_{n,predicted}$  values is achieved, and none of the  $r_m$  values are negative, nor nonsensical (for example  $r_2 > r_3 < r_4$  implies that sulfur rank 3 has a lower population than sulfur rank 2 and sulfur rank 4, which makes no logical sense).
- 15. Express the r<sub>m</sub> values as percentages of the sum of all r<sub>m</sub> values. The percentages obtained indicate what percentage each sulfur rank makes of the whole population. If desired, the average sulfur rank can easily be calculated from these percentage populations.

## XIX: DIB Case Study Band Deconvolution Data

Polymer	Centre Gravity / cm <sup>-1</sup>	Normalised Area	FWHM / cm <sup>-1</sup>
DIB50-S50-T135-0hr	378.45	0.2460	38.54
	441.09	1.0000	45.27
	464.90	0.6329	22.70
	493.72	0.7515	39.65
	535.39	0.1317	24.10
	433.00	0.0789	66.78
	474.41	0.6371	16.45
DIB50-S50-T135-2hr	383.73	0.4285	44.06
	428.88	0.3276	29.03
	462.28	1.0000	36.38
	500.25	0.6316	37.12
	536.08	0.1328	24.01
	433.00	0.0321	57.21
	473.18	0.2684	16.96
DIB50-S50-T135-	384.78	0.4249	39.91
Overnight	436.13	0.9077	40.59
	465.89	1.0000	28.18
	499.13	0.7110	32.37
	534.01	0.1717	23.03
	433.00	0.0592	57.93
	474.09	0.4880	17.05
DIB50-S50-T180-0hr	363.89	0.0688	20.68
	391.64	0.1903	17.56
	431.25	0.6908	34.42
	465.42	1.0000	29.01
	497.92	0.6920	25.13
	532.90	0.1645	23.09
	435.00	0.0247	36.62
	474.85	0.2073	16.30
DIB50-S50-T180-2hr	367.91	0.1115	23.29
	391.66	0.2742	17.61
	431.03	0.7371	36.59
	465.52	1.0000	30.30
	498.30	0.7382	24.83
	531.42	0.1873	25.15
	435.00	0.0299	25.07
	474.55	0.2478	17.05
DIB50-S50-T180-	365.86	0.1029	22.00
Overnight	391.59	0.3026	18.26
	431.19	0.7514	36.02
	465.36	1.0000	29.66
	498.64	0.7776	24.30
	532.09	0.1936	23.41
	433.00	0.0325	24.55
	474.93	0.2652	16.55

**Table S4**: Band deconvolution data for DIB polymers synthesized under different conditions. Values in orange are for elemental sulfur

#### XX. DIB Case Study

In order to prove that Raman spectroscopy can have useful applications outside of the proof-of-concept examples already mentioned, Raman analysis was used to analyse inverse vulcanised polymers of DIB. DIB polymers have been observed to have different properties depending on the reaction temperature and curing time. For example, when DIB polymers are synthesized at high temperature (180 °C), they rapidly vitrify into a hard, high  $T_g$  glass. However, if they are cured for longer, the  $T_g$  reduces, and the DIB polymers can become more like a viscous, sticky liquid. As such, Raman spectroscopy was employed to explore the reasons for these observations. DIB50-S50 polymers were synthesized by the general method described before, but this time they were reacted at either 135 °C or 180 °C, and then either not cured at all, or cured at 135 °C for 2hr or overnight. This gave the following notation: DIB50-S50-T $\gamma$ - $\Delta$ , where  $\gamma$  is the temperature of reaction in °C, and  $\Delta$  is the curing time of either 0 hours, 2 hours, or overnight. These polymers were subsequently analysed by Raman spectroscopy, the results of which can be seen in Figure S54.



Figure S54: The Raman spectra of DIB polymers, synthesized and cured under different conditions. All spectra were obtained under a laser power of 430 mW (100%), with the following integration times: DIB50-S50-T135-0hr 500 ms; DIB50-S50-T135-2hr 500 ms; DIB50-S50-T135-Overnight 200 ms; DIB50-S50-T180-0hr 1500 ms; DIB50-S50-T180-0hr 1500

As can be seen in Figure S54A and Figure 54B, there is a marked difference between the spectra of DIB polymers synthesized at 135 °C and 180 °C. One of the most noticeable differences is that polymers synthesized at 180 °C show much less fluorescence than polymers synthesized at 135 °C. This influenced the integration times used to obtain the spectra, as the polymers synthesized at 180 °C were obtained with much longer integration times, as there was less concern of the signal swamping out the detector with the fluorescent background. A study performed by Onose *et al.* suggested that the colour of some polymers may result from the formation of 1,2-dithiole-3-thione rings as terminal functionalities. Their work suggested that prolonged heating of such polymers, such as that experienced during the curing step, can result in greater populations of 1,2-dithiole-3-thione termination products.<sup>7</sup> Since these ring structures absorb visible light, they could be responsible for polymer fluorescence, and so could explain why DIB polymers that are cured for longer, show greater fluorescent backgrounds. This would also suggest that when DIB polymers are synthesized at high temperature, the reaction pathway that produces 1,2-dithiole-3-thione products, is suppressed or outcompeted. Thus, in the future, the behaviour of 1,2-dithiole-dithiones in relation to this Raman analysis should be investigated through a combination of experimental and computational methods.

Interestingly, for both the polymers synthesized at 135 °C and 180 °C, a two-hour curing time results in a significant reduction in Raman signal through the fluorescent background. This is surprising, as it suggests that fluorescence increases and then decreases as the curing step proceeds, though it is difficult to explain this without detailed understanding of the origin of the fluorescence. The intensity of the aromatic signals in comparison to the sulfur – sulfur band does not change much over the course of the reaction, which suggests that the proportion of crosslinker does not change much as curing proceeds, though this conclusion is complicated by the fact that different sulfur ranks give different intensities to the sulfur – sulfur band, meaning the intensity of the sulfur – sulfur band will change as a function of sulfur rank and not just the crosslinker proportion. For this reason, Raman analysis is not recommended for quantitatively assessing the proportion of crosslinker in a polymer.

Observing Figure S54A the intensity at about 500 cm<sup>-1</sup> increases as the curing process proceeds, which indicates an increase in the proportion of rank 2 chains. This conclusion agrees with previous conclusions from the DVB curing experiments. These data suggest that as the curing step proceeds, longer sulfur rank chains are consumed and broken down, and the sulfur atoms are distributed into more shorter sulfur rank chains. Note that the band deconvolution data in the supporting information, Section XIX, does not at first glance, seen to support this conclusion, but this is because the Gaussians are not centred on 500 cm<sup>-1</sup> and also have varying FWHM values. This conclusion is also supported by the fact that Figure S54A shows that the intensity at about 380 cm<sup>-1</sup> goes up as the curing time increases, and this may be due to an increase in the number of rank 3 chains, in accordance with Figure 9. Overall, the data in Figure S54A suggests that the sulfur rank decreases as expected as curing proceeds.

Figure S54B shows that DIB polymers synthesized at 180 °C are drastically different to analogous polymers synthesized at 135 °C. For instance, band deconvolution of the sulfur – sulfur band indicated that DIB polymers synthesized at 135 °C could have the sulfur – sulfur band accurately fitted by only five Gaussian peaks (excluding those for elemental sulfur) whereas polymers synthesized at 180 °C needed six Gaussian peaks to accurately describe their sulfur – sulfur band (again, excluding the peaks for elemental sulfur). It seems that in Figure S54B, the peaks at about 460 cm<sup>-1</sup> are weaker than the 460 cm<sup>-1</sup> peaks in Figure S54A, and so the other peaks in Figure S54B seem stronger in comparison to the 460 cm<sup>-1</sup> peak, than the analogous peaks do in the Figure S54A spectra. The 460 cm<sup>-1</sup> peak may receive contributions from all sulfur ranks, much like Group 4 in Figure 9, and if this is the case, it suggests that there may be a higher proportion of longer sulfur ranks present. Figure 9 helps to explain this justification, as it suggests that most sulfur ranks contribute very similar intensities to Group 4, but progressively longer sulfur ranks contribute progressively greater intensities outside of Group 4. According to Figure 9, the 392 cm<sup>-1</sup> peak may correspond to sulfur rank 3, and according to the band deconvolution data in Section XIX. of the supporting information, this peak gains intensity as the curing proceeds, again supporting the previous conclusion that he sulfur rank shortens with increasing curing. Additional evidence to this is the gain in intensity at 498 cm<sup>-1</sup> and the gain in intensity at 532 cm<sup>-1</sup> as curing proceeds. Thus, it can be concluded that the longer the curing time, the shorter the sulfur rank becomes, and that, the higher the initial reaction temperature, the higher the sulfur rank, which is in line with the well-established theory that elemental sulfur forms longer homopolymer chains at higher temperatures, and since it is these homopolymers that initially connect the crosslinkers together, a higher sulfur rank results. Further computational studies may be required to fully understand why the sulfur - sulfur band of DIB polymers synthesized at low and high temperature are so different.

## XXI. References

- 1. S. W. Bishnoi, C. J. Rozell, C. S. Levin, M. K. Gheith, B. R. Johnson, D. H. Johnson and N. J. Halas, *Nano Lett.*, 2006, **6**, 1687-1692.
- 2. L. Vigderman and E. R. Zubarev, Chem. Mater., 2013, 25, 1450-1457.
- 3. B. Chase, B. Anal. Chem., 1987, 59, 881A.
- 4. L. Cabo-Fernandez, A. R. Neale, F. Braga, I. V. Sazanovich, R. Kosteckic and L. J. Hardwick, L. J., *Phys. Chem. Chem. Phys.*, 2019, **21**, 23833-23842.
- 5. L. J. Dodd, O. Omar, X. Wu and T. Hasell, ACS Catal., 2021, 11, 4441–4455.
- 6. S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456–1465.
- 7. Y. Onose, Y. Ito, J. Kuwabara, and T. Kanbara, Polym. Chem., 2022.