Electronic Supplementary Information

Processes for coating surfaces with a copolymer made from sulfur and dicyclopentadiene

Maximilian Mann,^a Bowen Zhang,^b Samuel J. Tonkin,^a Christopher T. Gibson,^c Zhongfan Jia,^a Tom Hasell^{*b} and Justin M. Chalker^{*a}

- a. Flinders University, Institute for Nanoscale Science and Technology, College of Science and Engineering, Bedford Park, South Australia 5042, Australia
- b. Department of Chemistry, University of Liverpool, L69 7ZD United Kingdom
- c. Flinders Microscopy and Microanalysis, College of Science and Engineering, Flinders University, Bedford Park, Adelaide, South Australia, 5042 Australia
- E-mail: T.Hasell@liverpool.ac.uk

E-mail: justin.chalker@flinders.edu.au Web: www.chalkerlab.com

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General Considerations

Materials: Dicyclopentadiene (DCPD) was purchased from Sigma-Aldrich. Sulfur was purchased from Sigma-Aldrich (reagent grade, powder, purified by refining, 100 mesh particle size). Silica gel was purchased from Sigma-Aldrich (technical grade, pore size 60Å, 230-400 mesh particle size, 40-63 µm particle size).

Simultaneous thermal analysis (STA) was performed using a Perkin Elmer STA 8000. Between 5-10 mg of sample were held at 40 °C for 4 minutes before the temperature was increased by 10 °C/minute to 800 °C. This was done under a 20 mL/min nitrogen flow.

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 8000. Between 5-10 mg of sample was cooled to -80 °C and held for 4 minutes. After that the temperature was increased to 80 °C by 10 °C/minute and held for 4 minutes. Next, the sample was again cooled to -80 °C by 10 °C/minute and held for 4 minutes at that temperature. Finally, the sample was heated to 250 °C by 10 °C/minute. This was under a 20 mL/minute nitrogen flow.

¹**H NMR** spectra were recorded on a 600 MHz Bruker spectrometer with CDCl₃ as solvent. Spectra were referenced to residual solvent peaks (δ_{H} = 7.26 for CDCl₃).

Infrared (IR) spectra were recorded using a FTIR Perkin Elmer Frontier spectrometer between 4000 and 500 cm⁻¹. This was done by using the ATR technique or making a KBr disk. A KBr disk was fashioned by adding a small amount of sample (10-50 mg) to 200 mg of dry KBr. The sample was thoroughly mixed using mortar and pestle before being pressing onto a disk using pressures of around 10 tons.

SEM and EDX images were obtained using a FEI Inspect F50 SEM fitted with a EDAX energy dispersive X-Ray detector. Samples were sputter coated with silver metal (20 nm thickness) before analysis.

Cold vapour atomic absorption spectroscopy (CVAA) was carried out by a commercial service. Briefly, aqueous samples were digested using bromine monochloride (BrCl) before Cold Vapour Atomic Absorption spectroscopic analysis using a method adapted from the following standard methods: APHA 3112 (USEPA 7471A & USEPA 1631 Rev E).

CHNS elemental analysis was performed by The Campbell Microanalytical Laboratory at the University of Otago in New Zealand.

Gel permeation chromatography (GPC) was performed using a Shimadzu Prominence UPLC fitted with a Phenomenex Linear (2) column with matching guard column and a refractive index detector. The analysis was performed with a mobile phase of HPLC grade chloroform with 1% ethanol and an oven temperature of 40 °C. The flow rate was set to 1.00 mL/min. Polystyrene standards were used for calibration.

Laser desorption mass spectroscopy (LD-MS) was performed using a Bruker Autoflex III Smartbeam instrument. To collect the data a nitrogen laser with a wavelength of 355 nm was used and the instrument was set to reflectron mode.

Gas chromatography – **mass spectrometry (GC-MS)** was performed using an Agilent 7890A GC system fitted with an Agilent 5975C inert XL EI/CL MSD with triple-axis detector and Agilent 7693 autosampler. The column used was an Agilent J&W HP-4ms GC Column, 30 m, 0.25 mm, 0.25 μ w, 7 inch cage (19091S-433). The initial temperature of 30 °C was held for 3 minutes before ramping by 20 °C / min to 200 °C. The gas flow rate (helium) was 1.2 mL

/ min. The injection volume was 1 μ L with a 60:1 split ratio. The total run time was 21.5 minutes. As calibrations polystyrene calibrations were used.

Atomic force microscopy (AFM) images were acquired using a Bruker Multimode 9 AFM with a Nanoscope V controller using tapping mode in air, with all parameters including setpoint, scan rate and feedback gains adjusted to optimize image quality. In order to minimize tapping force amplitude set-points, during scanning, were kept at 80 to 90% of the cantilever free amplitude. As a result, no image or adhesion artefacts were observed in the AFM images indicating no tip contamination occurred due to the polymer surface.^{1, 2} The AFM probes used for all measurements were Mikromasch HQ: NSC15 Si probes with a nominal spring constant of 40 Nm⁻¹ and a nominal tip diameter of 16 nm. For the measurement of mechanical properties (elastic modulus and hardness) of the polymer the cantilever sensitivity and spring constant were calibrated using procedures outlined in Sader et al.³ The spring constant for cantilevers calibrated ranged between 23.8 to 34.6 N/m. The scanner was calibrated in x, y and z directions using a silicon calibration grid (Bruker model number VGRP: 10 µm pitch, 180 nm depth PG: 1 µm pitch, 110 nm depth, Mikromasch model TGZ01: 3 µm pitch, 18 nm depth).

Roughness analysis of AFM images was performed using Nanoscope analysis software version 2.0 and elastic modulus and hardness measurements were analysed using a combination of Nanoscope Analysis version 2.0 and the data analysis software Gwyddion version 2.59.

Samples for AFM were prepared by placing flat pieces of oligomer **1** in silicon wafers and curing them in an oven at 140 °C for 24 hours. Before AFM analysis each sample was gently rinsed with ethanol and dried with nitrogen gas.

Reaction of DCDP at 160 °C and 140 °C

This experiment was performed to assess if cyclopentadiene is formed when dicyclopentadiene (DCPD) is heated to 160 °C and if less CPD is formed during lower temperatures (140 °C). To do this 5.00 g of DCPD was added into a 100 mL round bottom flask fitted with a condenser. Then, the DCPD was heated to 140 °C or 160 °C respectively while being stirred for 2 hours before analysis by ¹H NMR (600 MHz, CDCl₃). Freshly cracked and distilled cyclopentadiene was also analysed by ¹H NMR for comparison:



¹H NMR spectrum of freshly cracked and distilled cyclopentadiene (CDCl₃, control spectrum)



¹H NMR spectrum of DCPD (CDCl₃, 600 MHz, control, no heating)



¹H NMR spectrum of DCPD after heating at 160 °C for 2 hours. The peaks at δ = 6.57 and 6.47 ppm are due to the vinylic protons of cyclopentadiene and the peaks between δ = 5.98 and 5.48 correspond to the vinylic protons of DCPD.

Result: 12% cyclopentadiene and 88% DCPD



¹H NMR spectrum of DCPD after heating at 140 °C for 2 hours. The peaks at δ = 6.57 and 6.47 ppm are due to the vinylic protons of cyclopentadiene and the peaks between δ = 5.98 and 5.48 correspond to the vinylic protons of DCPD.

Result: 3% cyclopentadiene and 97% DCPD



GC-MS chromatogram of DCPD and mass spectrum of eluent at 7.680 minutes.

Reaction of sulfur and DCPD, uncapped and unstirred in an oven at 140 °C

For this experiment 11 glass vials (20 mL) each containing 3.00 g of sulfur and 3.00 g of DCPD were prepared. The vials were placed in a 140 °C oven (uncapped) for times 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 24 hours. After the reactions were removed from the oven, phase separation was observed for samples reacted for 1 and 2 hours. Hence, these samples were not further characterised. The remainder of the samples were analysed using ¹H NMR.



Reaction of 3.00 g DCPD and 3.00 g sulfur at 140 °C in an oven for 1-24 hours directly after they have been removed from oven. Phase separation was observed for the 1 and 2 hour samples.



Reaction of 3.00 g DCPD and 3.00 g sulfur synthesised at 140 °C in an oven 24 hours. The image shows all samples after the final sample of 24 h reaction time was removed from the oven. Phase separation and crystalline sulfur was observed for reaction times of 1, 2, 3, and 4 hours.



¹H NMR spectra of the alkene region (in CDCl₃) of 3.00 g of DCPD and 3.00 g of sulfur after reacting in an uncapped 20 mL glass vial for 3 to 24 hours at 140 °C. The norbornene alkene of DCPD is completely consumed after 8 hours.



Glass transition temperatures (T_g) of the products of the reaction of 3.00 g of DCDP and 3.00 g, heated in an uncapped 20 mL vial in an oven at 140 °C for 8, 9, and 10 hours. This increase in T_g during curing is attributed to crosslinking via S-S metathesis and also addition of thiyl radicals to unreacted alkenes in DCPD.

Reaction of DCPD and sulfur at 140 °C under nitrogen with the addition of water

To two 20 mL glass vials, 3.00 g of DCPD and 3.00 g of sulfur were added. To one of the vials, 400 μ L of deionised water was added. The vials were then purged with nitrogen for 20 minutes, and then placed under 1 atm of nitrogen for the reaction (balloon). Following that, both reactions were stirred and heated to 140 °C for 2 hours. After this time, the reactions were cooled under nitrogen. The polymer formed in the presence of water is referred to as S-DCPD-H₂O. The polymer formed in the presence of water contained a fraction of material not soluble in CHCl₃:



55 mg of the products obtained above were mixed with 10 mL of chloroform. An insoluble fraction can be seen in the solution containing the product synthesised in the presence of water. The polymer synthesised under dry conditions was fully soluble in chloroform.

IR spectrum of the insoluble fraction of S-DCPD-A and S-DCPD-H $_2O$

To assess solubility of S-DCDP-A (polymer made under same conditions as oligomer **1** but open to air) and S-DCPD-H₂O, 500 mg of each polymer was placed in 15 mL of chloroform. After 1 hour the solvent was removed and replaced with another lot of 15 mL of chloroform. This process was repeated after an additional 100 hours and 200 hours. After the solvent had been removed the samples were dried under high vacuum for 24 hours.

Of the S-DCDP-A polymer 36% of its mass was not soluble under these conditions.18% of the mass of the S-DCPD-H₂O polymer was insoluble under these conditions. We attribute this insolubility to the interference of water in the reaction. When the polymer is formed under dry, conditions and an inert atmosphere, the product polymer is fully soluble in chloroform.



IR spectrum of insoluble material from a reaction open to air after 2 hours showing a broad C-H alkane stretch and a small C=C-H alkene stretch



Elemental analysis of S-DCPD-Air soluble and insoluble fractions

Optimised synthesis of oligomer 1

DCPD (3.00 g, 22.7 mmol) was added to a dry 20 mL glass vial followed by sulfur (3.00 g, 93.8 mmol) and a magnetic stirring bar. The vial was then sealed with a rubber septum and purged with nitrogen gas for 20 minutes and then maintained under a stream of nitrogen throughout the reaction. Next, the vial was placed in a hotblock pre-heated to 140 °C. The reaction was stirred (500 rpm) for 2 hours. Over this time the reaction mixture changes to a brown and then black viscous material. The reaction was then removed from the hotblock and cooled under a stream of nitrogen. After the material cools, the material appears as a black wax. This product can be stored in the vial for at least 8 months. The material can be removed from the vial by gently heating to soften the material, which can then be removed with a spatula or forceps.

NMR analysis of oligomer 1



¹HNMR of DCPD and oligomer **1** indicating partial consumption of alkenes between 5.5-6.5 ppm and the formation of C<u>H</u>S groups between 3.5-4.0 ppm.



¹³CNMR of DCPD and oligomer **1** showing the formation of new peaks due to C-S bond formation (60-75 ppm).



HSQC NMR of oligomer **1**. The cross-peaks for the signals between 60-75 ppm and the signals at 3.5-4.0 ppm are consistent with the formation of C-S bonds by the reaction of sulfur with dicyclopentadiene.

Thermal analysis of oligomer 1 and S-DCPD-A



DSC analysis revealed a T_g of 3 ± 1 °C for oligomer 1 a T_g of 10 ± 1 °C for S-DCPD-A.



STA analysis of oligomer **1** revealed two mass losses. The first one starting at around 160 °C. The second mass loss occurs above 250 °C.

GPC analysis of oligomer 1



GPC analysis of oligomer **1** was carried out for three independent syntheses. The average MW of these three syntheses was 1100 ± 100 g mol⁻¹ and the average Đ was 1.8. (This analysis was based on a polystyrene calibration)

Molecular weight monitoring in the preparation of oligomer 1

In an effort to find out how the molecular weight of oligomer 1 increased during the reaction time the following experiment was performed.

3 g of DCPD and 3 g of sulfur were placed in a 20 mL glass vial together with a stirrer bar. The vial was then purged with nitrogen for 20 minutes. After that the reaction was placed in a pre-heated 140 °C hot block for 2 hours while being stirred at 500 RPM and under nitrogen atmosphere. At 30, 60, 90 and 120 minutes reaction time a small amount of sample was removed using a syringe. These samples were prepared for GPC analysis with a concentration of 2 mg/mL in HPLC grade chloroform.



GPC analysis of the reaction mixture at 60, 90 and 120 minutes reaction time showed polymer with similar MW. The MW after 60 minutes was 950 g/mol, after 90 minutes it was 980 g/mol and after 120 minutes it was 980 g/mol. (This analysis was based on a polystyrene calibration)

At 30 minutes no polymer was present, so the MW analysis was only done after 60 minutes of reaction time. It was also noted that the dispersity increases with reaction time with D = 1.4 at 60 minutes, D = 1.7 at 90 minutes and D = 1.9 at 120 minutes due to an increase of higher molecular weight fractions.

LiAlH₄ reduction of uncured and cured oligomer 1

To cure the polymer, 200 mg of oligomer ${\bf 1}$ polymer was heated in an oven for 24 hours at 140 $^\circ C.$

For the reduction, 41 mg of either oligomer **1** or cured **1** were used. First, the samples and magnetic stirrer bars were added to two separate, flame dried 25 mL round bottom flasks. After that the reactions were purged with nitrogen for 20 minutes.

A LiAlH₄ solution (approximately 1M) was prepared by weighing 377 mg of LiAlH₄ while maintaining a nitrogen atmosphere in a 20 mL glass vial. Next, 10 mL of anhydrous THF was carefully added while under nitrogen. The solution was stirred for 10 minutes. Next, 2.5 mL of the LiAlH₄ solution was added to each reaction vessel using a glass syringe while maintaining a nitrogen atmosphere. Following that, the reactions were stirred for 24 hours.

After this time, both reactions were quenched using 5 mL of 1 M HCl. The acid was added slowly to accommodate the formation of hydrogen gas. After the reactions were quenched, 5 mL of cyclohexane were added to each reaction to extract the organic material. Following the cyclohexane addition, both reactions were stirred for 1 hour.

Lastly, the organic fraction of both reactions were separated using a 100 mL separating funnel and collected for analysis by GC-MS.





Gas chromatograph of the LiAlH₄ reduction of uncured oligomer **1**, indicating four major products at retention times of 7.68, 10.31, 10.38, and 12.58 minutes.



Mass spectrum of the peak at 7.68 minutes is consistent with that of DCPD. Because ¹H NMR indicated complete consumption of DCPD in the formation of **1**, we propose that highly basic LiAlH₄ can convert **1** to DCPD via an elimination reaction.



Mass spectrum of the peak at 10.31 minutes of the LiAlH₄ reduction of oligomer **1**. We propose that the hydride can break C-S bonds, resulting in the desulfurised product. Note only one possible regioisomer of the thiol is shown.



Mass spectrum of the peak at 10.38 minutes of the LiAlH₄ reduction of oligomer **1**. The proposed product could be a regio- or diastereoisomer of the compound associated with the peak at 10.31 minutes. (Only one potential regioisomer is shown).



Mass spectrum of the peak at 12.58 minutes of the LiAlH₄ reduction of oligomer **1**. This is the major product and the one expected to be formed upon reduction of the S-S bonds in **1**.



Mass spectrum of the of the peak at 16.1 minutes of the LiAlH₄ reduction of oligomer **1**. This cyclic product could form via intramolecular cyclisation during the reduction. This product could also be reduced further by reaction with LiAlH₄. For example:



Solubility studies of cured 1

To conduct the solubility studies approximately 100 mg of cured **1** was added to 3 mL of solvent. The following solvents were used: DMF, THF, NMP, chloroform, ethyl acetate, acetone, methanol, isopropanol and water. After 24 hours the polymers were removed from the solvents, rinsed with acetone and dried under high vacuum overnight. The weight of the polymers before and after their exposure to the solvents was recorded. No weight loss could be determined indicting the insolubility of cured **1** to all the solvents used.



Images of cured **1** in solvents at 0 hours (top) and after 24 hours solvent exposure (bottom).

Solvents: 1) DMF, 2) THF, 3) NMP, 4) Chloroform, 5) Ethyl acetate, 6) Acetone, 7) Methanol, 8) Isopropanol, 9) Water

AFM roughness analysis of cured 1

Small pieces of oligomer **1** were placed on a silicon wafer and placed in an oven at 140 °C to cure for 24 hours.

Thirteen 5 \times 5 μ m images were acquired on the polymer sample at distinctly separate locations (i.e. the tip was disengaged from the surface and moved some hundreds of microns in the X and Y directions before re-engaging). Average, R_a, and root mean square (RMS), R_g, roughness analysis was performed on each AFM image and an average taken with the error in the roughness measurements reported representing one standard deviation in the data. R_a and R_a roughness are standard analysis methods to report surface roughness using AFM. They differ in their mathematical description of roughness. Where R_g is the root mean square average of the height deviations taken from the mean image data line and R_a is the arithmetic average of the absolute values of the surface height deviations measured from the mean plane. In many instances they give different answers but do often follow the same trends between images as we observed in our case. However, one can infer from examination of their definitions and formulas, that a single large peak or flaw within the microscopic surface texture will affect (raise) the R_g value more than the R_a value. In our case, as mentioned, although we saw differences between the absolute values for the R_a and R_g roughness for each AFM image the overall trends for both types of roughness analysis were similar. For the AFM images acquired the average roughness $R_a = 0.37 \pm 0.07$ nm and the RMS roughness R_a = 0.92±0.36 nm. The image below in figure 1 is an example of one of the AFM topography images acquired on the polymer samples. While the roughness for the polymer over the regions examined is low compared to other polymers studied using AFM (e.g. R_a = 8.84 nm Tonkin et al⁴ and $R_a = 1$ to 4 nm Gibson et al⁵) there are present on the surface, in some images, some particles or imperfections range from 6 to 46 nm and have an average height of 16 ± 14 nm. These are indicated on the AFM image by red arrows.



Representative AFM image of the surface of cured **1**. Red arrows indicate small particles on the surface.

AFM analysis of modulus and hardness of cured 1

Mechanical measurements

AFM nanoindentation was used to determine the mechanical properties of the polymer which is important for the thin film applications of the polymer. However, research indicates that for homogenous samples data derived from nanoindentation can potentially yield useful information on the bulk material properties.⁶

Elastic modulus

For all surface mechanical measurements, the force spectroscopy section of the Nanoscope software was used for analysis. Approximately 25 force curves were acquired at several locations across the polymer surface. The force curves were converted to indentation curves and the Hertz model was used to determine the elastic modulus. The Hertz model approximates the AFM tip as a sphere contacting an elastic surface which serves as a good model for the tip-surface interaction in our measurements. The equation for the Hertz model is given below⁷

$$F = E \left[(4/3) R^{1/2} \delta^{3/2} (1-v)^{-1} \right]$$
(1)

Where E is the elastic modulus, F is the applied force determined by the calibration of the cantilever sensitivity and spring constant³ and extracted from the indentation curve, R is the AFM tip radius which is the nominal value provided by the manufacturer of 8 nm, δ is the indentation of the surface produced from the applied Force, F, and v is the Poission ratio which is approximated as 0.3 which is a value typical for polymers.⁸ The Nanoscope software fits a curve, using the Hertz model, to the indentation curve and from this the elastic modulus is determined as a fit parameter. A loading indentation curve (blue) with Hertz model fit (green) are shown in Figure 2. Only loading curves were analysed to determine the elastic modulus as outlined in Kontomaris et al.⁹ It was found that for applied forces less than 100 nN plastic deformation of the sample was minimized. This analysis resulted in a measured elastic modulus of 1.49 ± 0.36 GPa with the error in the measurement representing one standard deviation in the data. The elastic modulus is comparable to value reported for nylon, PVC and polycarbonate.¹⁰

Hardness

For surface area hardness measurements, the maximum applied force and the area of the indent made by the AFM tip must be determined. The equation for determining hardness is $below^7$

$$H = F_{max}/A_{indent}$$
(2)

Where H is the surface area hardness, F_{max} is the maximum applied force extracted from the force curve and A_{indent} is the area of the indentation produced by F_{max} . Approximately 25 force curves were acquired at several locations across the polymer surface with the maximum applied force ~ 2-2.5 µN. When the force curves were completed, typically over a 2x2 µm scan size, the areas were reimaged in tapping mode to produce the AFM images of the resulting indents. An example of an AFM image of a typical indent is shown in figure 3. The area of the indents, A_{indent} , was determined using the specialised indentation section of the online analysis software Gwyddion version 2.59 and was, on average, ~ 10,000 nm². This analysis resulted in a measured hardness of 0.25 ± 0.09 GPa and 25.9 ± 9.6 for the surface area hardness and Vickers hardness, respectively. The error in each measurement represents one standard

deviation in the data. This is comparable to hardness values reported for various polymers such as nylon, PMMA and polystyrene.^{10, 11}



Example indentation curve (blue) acquired on the polymer surface. The green curve is the Hertz model fit which, for this particular curve, yielded an elastic modulus of 1.74 GPa



Example AFM image of an indentation acquired in tapping mode.



GC-MS analysis of cured 1 after reduction with LiAlH₄

Gas chromatogram of the LiAlH₄ reduction of cured **1**. The product distribution is more complicated than for the reduction of oligomer **1**. We attribute this difference to additional crosslinking reactions via S-S metathesis of the polysulfide groups and also the reaction of the polysulfide with the unreacted alkenes in oligomer **1**. MS and proposed structures are provided for selected peaks on the subsequent pages.



Mass spectrum of the peak at 7.68 minutes of the LiAlH₄ reduction of cured **1**. We propose that highly basic LiAlH₄ can convert cured **1** to DCPD via elimination reactions.



Mass spectrum of the of the peak at 10.23 minutes of the LiAlH₄ reduction of cured **1**. C-S bond cleavage by the hydride is proposed to account for the putative structure.



Mass spectrum of the peak at 12.58 minutes of the LiAlH₄ reduction of cured **1**. The alkene of the putative structure may be from unreacted alkene after curing or the alkene could be formed via an elimination reaction.



Mass spectrum of the of the peak at 16.0 minutes of the LiAlH₄ reduction of cured 1.



Mass spectrum of the peak at 16.21 minutes of the LiAlH₄ reduction of cured **1**. The proposed structure is consistent with addition of sulfur groups to the unreacted alkene during curing process. C-S bond cleavage by the hydride is proposed to account for the odd number of sulfur atoms in the putative structure. Only one potential regio- and diasteroisomer is shown. For instance:




Mass spectrum of the peak at 16.65 minutes of the LiAlH₄ reduction of cured **1**. The structure proposed is tentative. It is not clear if the episulfide, if present, is formed during the curing process or in the reduction with LiAlH₄.



Mass spectrum of the peak at 17.35 minutes of the LiAlH₄ reduction of cured **1**. Note that this product could be a structural or diastereoisomer of the compound detected at 16.21 minutes (only one possible isomer is shown).

NaBH₄ reduction of oligomer 1

Oligomer **1** (41 mg) and a stirring bar were added to a flame dried 25 mL round bottom flask and purged with nitrogen for 20 minutes. The NaBH₄ solution (approximately 1M) was prepared by adding 381 mg of NaBH₄ in a 20 mL glass vial and placing under nitrogen. Next, 10 mL of anhydrous THF was carefully added while under nitrogen. The solution was stirred for 10 minutes. Next, 2.5 mL of the NaBH₄ solution was added to the reaction flask using a glass syringe while maintaining a nitrogen atmosphere. The flask was equipped with a condenser and then stirred at 20 °C for 3 hours, and then heated at 50 °C for an additional 2.5 hours. After this time, all of the solid material was in solution. Then, the reaction was returned to 20 °C and stirred for a total of 24 hours.

After this time, the reaction was cooled to room temperature and quenched with 5 mL of 1 M HCI. The acid was added very carefully and slowly so that the off gases generated could exit the flask. After the reaction was quenched, 5 mL of cyclohexane were added to extract the organic material. Following the cyclohexane addition, the mixture was stirred for 1 hour.

Lastly, the organic fractions of both reactions were separated using a 100 mL separating funnel and collected for GC-MS analysis.



GC-MS analysis of oligomer 1 after reduction with NaBH₄

Gas chromatograph of the NaBH $_4$ reduction of oligomer **1**. There was one major peak at 16.05 minutes.



Mass spectrum of the peak at 10.38 minutes of the NaBH₄ reduction of oligomer **1**. This minor product could potentially be formed after C-S bond cleavage by the reducing agent. Only one of the possible regioisomers is shown. For instance:





Mass spectrum of the of the gas chromatogram peak at 12.58 minutes of the NaBH₄ reduction of oligomer **1**. This is the expected product of complete reduction of oligomer **1**.



Mass spectrum of the of the gas chromatogram peak at 16.05 minutes of the NaBH₄ reduction of oligomer **1**. This is the major product of the reduction under these conditions. The cyclic trisulfide is proposed to form during the reduction:



Since the major product of the NaBH₄ reduction of the uncured oligomer **1** was the cyclic trisulfide, this material was purified and isolated by column chromatography, using 100 % hexane as the mobile phase. The GC-MS of the purified product is shown below.



Gas chromatograph of the purified dicyclopentadiene trisulfide



Mass spectrum of purified dicyclopentadiene trisulfide.



¹H NMR of cyclic trisulfide isolated after the reduction of oligomer 1 with NaBH₄

¹H NMR (600 MHz, CDCl₃). Note that this material may be a mixture of diastereomers. Key signals include δ = 5.73, 5.61 (H5 and H6), 3.70 (H1 and H9), 3.28 (H7), 2.70 (H3), 2.36 (H4 and H4'), 2.10 (H10), 1.32 (H10'), 1.26 (H2 and H8). HSQC and COSY were used in this tentative assignment.

 ^{13}C NMR of cyclic trisulfide isolated after the reduction of oligomer 1 with NaBH_4



 13 C NMR (125 MHz, CDCl₃): δ = 29.6 (C2 and C8), 31.7 (C4), 35.6 (C10), 40.5 (C3), 52.0 (C7), 62.7 and 66.2 (C1 and C9), 130.8 and 132.1 (C5 and C6)



COSY spectrum of isolated product (oligomer 1 NaBH₄ reduction)



HSQC spectrum of isolated product (oligomer 1 NaBH₄ reduction)

GC-MS analysis of cured 1 after reduction with NaBH₄

Oligomer **1** (838 mg) was cured at 140 °C for 24 hours. Cured **1** was ground up using a mortar and pestle and 514 mg of this material was added to a flame dried 100 mL two necked flask. NaBH₄ (1.190 g) was then added under a nitrogen atmosphere. A condenser was fitted to the flask while ensuring that the nitrogen atmosphere was maintained. To this reaction 20 mL of anhydrous THF was slowly added and then the reaction was heated to 50 °C and stirred for 48 hours. After this time, the reaction was quenched with 1M HCl and extracted into cyclohexane for analysis by GC-MS.



Gas chromatogram of the 500 mg cured **1** NaBH₄ reduction



Mass spectrum of the peak at 12.58 minutes



Mass spectrum of the peak at 16.00 minutes



Mass spectrum of the peak at 17.34 minutes. The proposed product requires reaction of the sulfur groups with the unreacted alkene during the curing process. Only one possible regioisomer is shown.

Reduction of cured 1 for chemical recycling study (4.4 g scale)

Cured **1** (4.4 g), NaBH₄ (9.68g) and a stirrer bar were added to a flame dried 1000 mL round bottom flask and purged with nitrogen for 20 minutes. After that dry THF (250 mL) was carefully added while under nitrogen. The flask was equipped with a condenser and then stirred at 50 °C for 24 hours while a nitrogen atmosphere was maintained.

After this time, the reaction placed in an ice-bath and quenched with w 1 M HCI. The acid was added very carefully and slowly so that the off gases generated could exit the flask. After the reaction was quenched, 150 mL of hexane were added to extract the organic material. Following the hexane addition, the mixture was stirred for 1 hour.

Lastly, the organic fractions of both reactions were separated using a 1000 mL separating funnel and collected for GC-MS analysis.



GC-Ms analysis of cured 1 after reduction with NaBH₄ (4.4 g reaction)

Gas chromatogram of the NaBH₄ reduction of cured **1**.



Mass spectrum of the of the peak at 10.38 minutes of the NaBH₄ reduction of cured **1**. C-S bond cleavage by the hydride is proposed to account for the putative structure.



Mass spectrum of the peak at 12.58 minutes of the NaBH₄ reduction of cured **1**. The alkene of the putative structure may be from unreacted alkene after curing or the alkene could be formed via an elimination reaction.



Mass spectrum of the of the gas chromatogram peak at 15.98 minutes of the NaBH₄ reduction of oligomer **1**. This is the major product of the reduction under these conditions. The cyclic trisulfide is proposed to form during the reduction:





Mass spectrum of the peak at 17.32 minutes of the NaBH₄ reduction of cured **1**.

After the organic material was extracted, the hexane was removed using a rotary evaporator. Next some of the sample was transferred into a silicon mould and dried under high vacuum overnight.

Re-curing 1 after reduction step of chemical recycling

After the sample was dried under vacuum, the sample was cured for 24 hours in an 140 °C oven. Before the curing process the sample had a waxy consistency. After the during process, the sample was hard and brittle.



STA of re-cured 1 after chemical recycling

STA analysis of cured **1** and cured **1** after reduction and subsequent curing. The first mass loss of cured **1** is around 250 °C whereas the reduced and re-cured sample has a mass loss at lower temperatures at around 225 °C. Further, after heating to 800 °C the reduced and cured sample lost a total of 72% of its mass which is 13% more than cured 1 which only lost 59% of its mass.



Elemental analysis of cured 1 (blue) and reduced and re-cured sample (red)

Cured 1 had higher sulfur content and lower carbon content compared to the reduced and re-cured product. We attribute this difference to loss of sulfur during the reduction.

Solubility test of the product formed after reducing and re-curing

To conduct the solubility studies approximately 100 mg of re-cured 1 was added to 3 mL of solvent. The following solvents were used: DMF, THF, NMP, chloroform, ethyl acetate, acetone, methanol, isopropanol and water. Immediately after the polymer was added to the solvents the polymer started to dissolve in THF, NPM and chloroform. After 30 minutes all the polymer had dissolved in THF and chloroform. At 60 minutes the polymer had dissolved in NMP. The polymer in DMF began do dissolve after around 1 hour and after 24 hours 60% by weight had dissolved. Limited solubility (1.4 % by mass) was observed in acetone. Under these conditions, the re-cured product was not soluble in ethyl acetate, methanol, isopropanol, or water.



Images of cured **1** in solvents at 0 hours (top) and after 24 hours solvent exposure (bottom). Solvents: 1) DMF, 2) THF, 3) NMP, 4) Chloroform, 5) Ethyl acetate, 6) Acetone, 7) Methanol, 8) Isopropanol, 9) Water

Silica gel coating with oligomer 1, curing process and chloroform wash

To coat silica gel, 1.66 g of oligomer **1** was dissolved in 150 mL of chloroform in a 250 mL round bottom flask before 16.6 g of silica gel was added. After stirring the solution for 20 minutes the solvent was removed by rotary evaporation. To cure oligomer **1** on the silica gel, the coated silica gel was placed in a 140 °C oven for 24 hours. To wash the cured coated silica gel, 15 mL of chloroform were added to 2 g of coated and cured silica gel. The washing process involved filtering the silica gel using vacuum filtration, recovering the silica gel and placing it back in the glass vial before the next 15 mL of chloroform were added. Then, the mixture was briefly stirred, and the filtration process was repeated. The washing process was performed 8 times. An image of the coated silica and the chloroform is shown below for each wash:



Washing of silica gel after coating with oligomer **1** and curing. The washing was done 8 times with 15 mL of chloroform in each wash, showing that the curing process rendered the polymer coating insoluble. It should be noted in the first three washes there is some trace soluble material (indicated by the darker liquid phase), but the remaining cured polymer was not removed from the silica after repeated washing.

The final coated silica gel was recovered by filtration, air dried, and then evaluated in mercury sorption.

Mercury uptake of oligomer 1 coated silica gel (cured and uncured)

First, silica gel was coated with oligomer **1** as previously described. A 14 g portion of the coated silica gel was cured in an oven at 140 °C for 24 hours. Following that, 2 g of the cured oligomer **1** coated silica gel was washed with 7 aliquots of 15 mL chloroform as described above.

Next, 45 mL of a 5 ppm aqueous solution of $HgCl_2$ was added to each of 13 separate 50 mL plastic tubes. One of these solutions served as control with no silica gel added to monitor the Hg concentration. The following experimental samples were then prepared in triplicate:

- a) 100 mg of uncoated silica gel was added to 45 mL aqueous HgCl₂ (5 ppm)
- b) 100 mg of the silica gel coated with uncured oligomer 1 was added to 45 mL aqueous HgCl₂ (5 ppm)
- c) 100 mg of the silica gel coated with cured **1** (not washed with CHCl₃) was added to 45 mL aqueous HgCl₂ (5 ppm)
- d) 100 mg of the silica gel coated with cured **1** (washed with CHCl₃) was added to 45 mL aqueous HgCl₂ (5 ppm)

After the silica gel was added the samples were rotated at 25 RPM for 2 hours. Samples for analysis were taken before the silica gel addition and at 0.5, 1.0, 1.5 and 2 hours. Samples were taken by removing 1 mL of solution and centrifuging the sample to separate the silica gel from the sample. Then, 0.7 mL of sample was stabilised in 5 % HCl and made up to a volume of 7 mL. The samples were analysed using CVAAS. The results are plotted on the following page.



Mercury uptake experiments showed a **a**) stable mercury solution if not sorbent was added to the solution, **b**) only 14 % of mercury removed by silica gel alone, **c**) a mercury uptake of 99% over 2 hours for the silica gel coated with uncured **1**, **d**) a 92% mercury uptake using the silica gel coated with cured oligomer **1** (unwashed), and **e**) a 93% mercury uptake when the silica gel was coated with cured **1** coated and washed with chloroform.

Isotherm absorption of silica gel coated with 1 and cured

Isotherms of silica gel coated with cured **1** were performed.

Firstly a 1000 ppm Hg solution was made by dissolving 136.4 mg of $HgCl_2$ in a 100 mL volumetric flask in deionised water.

For the isotherm, 5 samples with different Hg concentrations (4 ppm, 8 ppm, 12 ppm, 16 ppm and 20 ppm,) and volumes of 50 mL were prepared in triplicate in plastic tubes. To each sample 200 mg of silica gel coated with cured **1** was added. The samples were then rotated on an end-over-end mixer at 25 RPM for 7 hours. Following that an aliquot of each sample was filtered using a 0.45 μ m nylon syringe filter and the mercury concentration determined using CVAA as previously described.

For the isotherm fitting the Langmuir model was used:

$$q_{eq} = \frac{Q_{max}K_LC_{eq}}{1 + K_LC_{eq}}$$

Adsorption isotherm of mercury onto sample of silica gel coated with cured **1** using Langmuir isotherm fitting (red line). The maximum mercury capacity was 5 mg/g of sorbent.

Mercury uptake from a diesel-water mixture using silica gel coated with cured 1

First, a 384 ppm Hg solution was made by dissolving 52 mg of HgCl₂ in a 100 mL volumetric flask and diluting to the mark with deionised water. Next, three 45 mL samples with a Hg concentration of 5 ppm were prepared in 50 mL plastic tubes. This was done by adding 586 μ L of the 384 ppm mercury solution, 22.5 mL of deionised water and 22.5 mL of diesel fuel. Following that, 100 mg of the coated silica gel was added (coated with **1** and cured, as previously described, 10:1 mass ratio of silica to polymer). Then, the samples were shaken for 20 seconds to mix the contents before they were rotated at 25 RPM for 2 hours. Samples were taken at 0, 0.5, 1, 1.5 and 2 hours by removing 1 mL the aqueous phase and centrifuging the sample to ensure separation from the diesel. Finally, 0.7 mL of the aqueous samples were diluted to 7 mL in 5 % HCl and then analysed by CVAAS.



Before mixing

After mixing

Mixture of equal volumes of diesel fuel and water before and after end-over-end mixing, illustrating the emulsion that forms.



Hg uptake from a diesel/water mixture containing 5 ppm of Hg using silica gel coated with cured oligomer **1.** Over 92 % of mercury was removed within 2 hours.

Acid resistance studies for cured-1

To conduct the acid resistivity studies, 57 - 77 mg of cured **1** was added to 3 mL of undiluted acid. The following acids were used: HCl, H₂SO₄, HNO₃, TFA, H₃PO₄, and acetic acid. After 24 hours the polymers were removed from the acids, rinsed with deionised water and dried under high vacuum overnight. The weight of the polymers before and after their exposure to the solvents was recorded. Only two acids showed any effect on the polymer. Sulfuric acid dissolved 3% of cured-**1** in 24 hours and nitric acid dissolved 6% in 24 hours. This could also be seen in the discoloration of the acids 24 hours after the polymer as added.



Images of polymer in acids at 0 hours (top) and after 24 hours solvent exposure (bottom). Acids: 1) HCl, 2) H₂SO₄, 3) HNO₃, 4) TFA, 5) H₃PO₄, 6) Acetic acid

HCI treatment of cured 1

First, 1.0 g of oligomer **1** was dissolved in 2 mL of chloroform, with stirring for 1 hour to ensure complete dissolution. Next, the surface of four 1cm x 1cm aluminium pieces were covered with the oligomer **1** solution. The samples were left overnight to allow the majority of the solvent to evaporate. The samples were then placed in an oven pre-heated to 140 °C, followed by curing for 24 h. After that time, the oven was turned off so that the samples could cool down slowly. The aluminium pieces were weighed before the addition of the polymer solution and after the curing process to determine the weight of the polymer coating. The average polymer coating mass was 29.8 \pm 0.7 mg.

Next, 5 μ L of HCl (37%) were added to the surface of cured coating and left for 3 hours. After this time, the acid was washed off with water and the sample was gently dried with a paper towel. In addition, a chip of cured **1** was added to vial containing 5 mL of HCl and left for 24 hours. As a control, 5 μ L of acid were place on a piece of aluminium to document the corrosion after 3 hours.



a, **b**, **c**) Aluminium pieces coated with cured **1** and 5 μ L of HCl on the surface. **d**, **e**, **f**) Aluminium pieces coated with cured **1** after acid has been washed off. No damage or reaction was observed.



a) Aluminium piece before 5 μ L of HCl (37%) were added on top. **b)** Aluminium piece after 3 hours of HCl exposure, indicating significant corrosion. **c)** 8 mg of cured **1** submerged in 5 mL of HCl (37%) **d)** 8 mg of cured **1** after 24 hours in 5 mL of HCl (37%). No degradation or reaction of cured **1** was observed.

Coating cement with cured 1

Gyprock[™] Cornice Cement was mixed with water as per instructions and poured into a 8.5 cm long, 5.5 cm wide and 1.0 mm deep mould. After the cement had dried for 24 hours it was removed from the mould and cut into 1.5 cm long and 1.0 cm wide pieces resulting in a surface area of 1.5 cm². Next, a polymer solution was prepared by dissolving 1.0 g of oligomer **1** in 2 mL of chloroform. A 100 µL aliquot of that polymer solution was placed on the surface of a cement sheet and the solvent was allowed to evaporate. This procedure was repeated twice more (3 × 100 µL polymer solution in total) to ensure an even and complete coating of oligomer **1** on the cement surface. The coated cement sheet was then cured for 24 hours at 140 °C.

To test acid resistance after curing, 25 μ L of HCI (37%) was placed on the cement sheet coated with cured **1**. As a control the same was done to an uncoated cement sheet. Additionally, a 25 μ L aliquot of water was placed on a third cement sheet.



Top: Cement sheets directly after the water or HCI (37%) was added to the surface. Foaming on the surface of the uncoated cement sheet was observed for the sample treated with acid, indicated a chemical reaction. No reaction was observed during the acid treatment of the coated cement sheet.

Bottom: Cement sheets after 2 hours exposure to water or HCI. The water or acid on the surface of the uncoated cement sheets had been absorbed. No absorption or damage caused by the acid on the coated cement sheet.

Lining PVC pipe with cured 1 for solvent resistance

To coat the inside of a PVC pipe, 6.0 g of oligomer **1** was placed on baking paper on top of a hotplate. Upon warming (approximately 40 °C), oligomer **1** softens and can be rolled flat with a metal rolling pin. A sample approximately 7 x 7.5 cm was prepared by this method. The polymer film was then rolled around a cylindrical silicone insert (7 cm tall, 2.1 cm diameter). The silicon cylinder with the polymer wrapped around it was then placed into the PVC pipe (2.4 cm internal diameter, 6.5 cm length). The polymer filled the gap between the silicone insert and the PVC pipe; the polymer was in direct contact with the PVC. The PVC pipe, polymer film, and silicone insert were then secured in an aluminium mould to help maintain the shape of the PVC pipe. The full assembly was cured in an over at 140 °C for 24 hours.



a) A thin polymer mat was rolled around a silicone cylinder and placed into a PCV pipe. **b)** The PVC pipe containing the oligomer **1** mat around the silicon cylinder was placed in an aluminium mould. **c)** The whole assembly was then cured at 140 °C for 24 hours.

After the curing was completed, the assembly was removed from the oven and allowed to cool to room temperature. Next, the silicon cylinder was removed using pliers. The coated PVC pipe was then cut to a length of 3 cm. This was done by first heating the blade of a hacksaw with a Bunsen burner. Using the hot blade, the pipe was carefully cut so as to not damage the polymer coating.

To test solvent resistance, a separatory funnel was set up so that a steady flow of 5 mL/min of THF was able to pass through the pipe. Using this set up a total of 600 mL of THF was passed though both the uncoated and cured **1** coated PVC pipe over 2 hours.



A separator funnel was set up so that a steady flow of 5 mL/min of THF could pass though the uncoated PVC pipe.


After 600 mL of THF were passed though the uncoated PVC pipe substantial damage to the pipe could be seen.



Image of the uncoated PVC pipe next to the beaker of THF that was passed thought the pipe. The THF has a cloudy white appearance resulting from the dissolved PVC.



After 600 mL of THF were passed though the cured **1** coated PVC pipe no damage could be seen.



Image of the PVC pipe coated with cured **1** next to the beaker of THF that was passed through the pipe. The THF remained clear indicating that no coating or PVC was dissolved.

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